SEVENTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY,

LONDON, MAY 27TH TO JUNE 2ND, 1909.

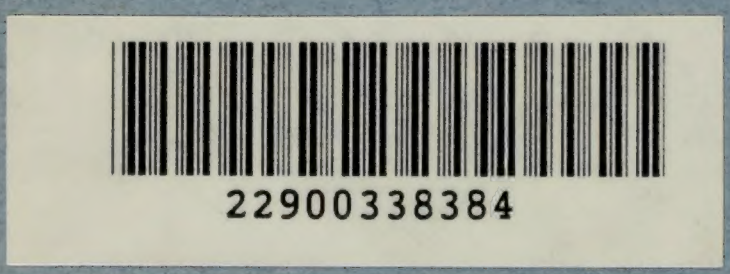
SECTION IX.

PHOTO-CHEMISTRY, PHOTOGRAPHY.

PUBLISHED BY
PARTRIDGE & COOPER, Ltd.,
191-192, FLEET STREET, LONDON, E.C.

1910.

K1086


22900338384

SEVENTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY,

LONDON, MAY 27TH TO JUNE 2ND, 1909.

SECTION IX.

PHOTO-CHEMISTRY. PHOTOGRAPHY.

Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S.

(Acting President of the Congress)

AND

WILLIAM MACNAB (*Hon. General Secretary*),

ASSISTED BY

H. CHAPMAN JONES.

PUBLISHED BY

PARTRIDGE & COOPER, LTD.,

191-192, FLEET STREET, LONDON, E.C.

1910.

13362

Copyright.

Entered at Stationers' Hall.

WELLCOME INSTITUTE LIBRARY
Coll. welMOmec
Call No. QD

SECTION IX.

PHOTO-CHEMISTRY. PHOTOGRAPHY.

President.

SIR W. DE W. ABNEY, K.C.B., F.R.S.

Vice-Presidents.

M. L. P. CLERC, *Paris.*
PROF. DR. R. LUTHER, *Dresden.*
PROF. R. NAMIAS *Milan.*
M. A. SEYEWETZ, *Bron (Rhône).*
SIR H. TRUEMAN WOOD, *London.*

Hon. Secretary.

H. CHAPMAN JONES, *Royal College of Science, South Kensington.*

Committee.

GEO. E. BROWN, *London.*
JAMES CADETT, *Ashstead.*
E. HOWARD FARMER, *London.*
C. E. KENNETH MEES, *London.*
PROF. R. MELDOLA, F.R.S., *London.*
A. J. NEWTON, *London.*
E. SANGER-SHEPHERD, *London.*
JOHN SPILLER, *London.*
SIR JOSEPH W. SWAN, F.R.S., *London*
PROF. J. M. THOMSON, LL.D., F.R.S., *London.*
GENERAL J. WATERHOUSE, *London.*

Digitized by the Internet Archive
in 2016

https://archive.org/details/b28122185_0015

CONTENTS.

PAGE

Address by Sir W. de W. Abney, K.C.B., F.R.S. 7

Etude comparative du Pouvoir Réducteur des principaux Révélateurs organiques et des moyens permettant d'augmenter ou de diminuer avec chacun d'eux les contrastes de l'image développée. MM. A. et L. Lumière et A. Seyewetz 9

Influenza dell' aggiunta di forti quantità d' Acido Borico sulla conservazione e comportamento del bagno di sviluppo al diamidofenolo. Prof. R. Namias 11

Recherches analytiques sur l'altération du Sulfite de Soude en présence de différents révélateurs et d'autres substances qui peuvent entrer dans les bains développateurs. Prof. R. Namias 14

Sur les Propriétés révélatrices du Pyramidol. M. L. P. Clerc 15

Discussion 15

Observations sur les Bains de Virage à l'Or à base de Sulfourées Prof. R. Namias 18

Discussion 18

Substitution de composés du Plomb et d'autres métaux à l'Argent des images sur plaques ou films au gélatino-bromure et leur utilisation comme mordants pour la teinture. Prof. R. Namias 19

Discussion 20

Die Wirkungsweise des Ammonium-Persulfats. J. Hertzberg 21

Discussion 21

Photographic Demonstration of Light Absorption. L. H. Friedburg ... 22

Ueber die latenten Bilder der Röntgenstrahlen und anderer Energiearten. Dr. Lüppo-Cramer 25

Discussion 27

The Reversal of the Photographic Image. Wilder D. Bancroft 27

Différents effets des sensibilisateurs sur les Plaques sensibles selon les propriétés du Bromure d'Argent de l'émulsion. S. de Prokoudine-Gorsky 28

Discussion 29

Photo-Chemical Deterioration of Oil Paintings. Maximilian Toch ... 30

Abstract of the Report on the present Condition of Sensitometry. C. E. Kenneth Mees, D.Sc. 35

Discussion 36

An International Standard Method of Marking the Speed of Photographic Dry Plates, and Definitions of the Standard Conditions under which such Speed Tests are to be carried out. F. W. T. Krohn 39

Discussion 45

On the Eder Solution. Dr. Chr. Winther 46

The Present Condition of Etching. A. J. Newton 50

Discussion 58

Abstract of the Report on Acid Resists. W. Gamble 58

PAGE

Discussion 59

Abstract of the Report on Colloid Chemistry in Relation to Photography. S. E. Sheppard, D.Sc. 60

Discussion 61

The Use of Agar-Agar in Photography. W. F. Cooper, B.A. (Cantab.), F.C.S., W. H. Nuttall, F.I.C., F.C.S., and G. A. Freak, B.Sc., A.I.C. 62

Discussion 71

On Gelatose and the cause of certain Variations in the Sensitiveness to Light of Mixtures of the Substance with Alkali Bichromates. Charles W. Gamble 73

The Action of Chromium Salts upon Gelatine. Charles W. Gamble ... 76

References 81

Photographic Films of Nitro-Cellulose. Henry M. Reichenbach ... 82

Sur un important perfectionnement apporté, par M. Danesi, aux méthodes et aux machines pour la photocollographie. Prof. R. Namias... ... 84

Congrès International de Photographie, Bruxelles, 1910. MM. R. Namias et L. P. Clerc 86

Présentation d'un album d'illustrations de Messnai et Reggio, Calabria. Prof. R. Namias 87

Aids to Photo-Micrography with Radiations of Short Wave-length. W. N. Hartley, D.Sc., F.R.S. 88

Postscript 94

Sur le traitement simplifié des plaques autochromes et la correction des erreurs de temps de pose au cours du développement. MM. A. et L. Lumière et A. Seyewetz 95

Discussion 95

Autochromes and their reproduction on Paper. Howard Farmer ... 97

Discussion 98

Address by Sir W. de W. Abney, K.C.B., F.R.S.

One of the most pleasing of my duties as President of this section is to welcome most heartily, on behalf of their British *confrères*, those members who have come from over the seas to attend the present Congress, and who have contributed so largely to the papers that are to be read and discussed. For the convenience of the meetings, and to save time, of which there is none too much, papers treating of kindred subjects have been grouped together, and where possible it is proposed that the discussion will be on the group of papers and, as a rule, not on the individual papers. But, of course, it will be in the power of the section to discuss an individual paper by itself—the bureau in this respect is in the hands of the meeting.

There are many other subjects, of course, which might be taken, and there is one to which, during some years, I have devoted a large amount of attention, namely, the use of photography for obtaining quantitative results. Where used in physical or astronomical observation I may observe that such use of photography involves a study of what I may call its "eccentricities." For instance, the photographic plate has to be studied in regard to the variation that may take place in the developed image when the exposure takes place under the influence of strong and weak lights, under the influence of various temperatures during exposure and development, under the influence of recurrent exposures, and so on—all such matters have to be taken into consideration when photography is used to take the place of, or supplement, eye observation, and I will go so far as to say that in obtaining an accurate idea of the speed of plates these "eccentricities" have to be taken into account.

In a recent research on fluorescence which I undertook the aid of photography has had to be invoked for the quantitative measurement of the spectrum colours which combine together to give the fluorescent colour. Fluorescence may be perfectly bright where a body is caused to fluoresce by throwing a brilliant spectrum upon it, but it is a very different matter when an amount of the fluorescent light has to pass through the slit of a second spectroscope and itself be analysed. The spectrum given is very feeble, and owing to the inherent incapacity of the eye to distinguish and measure accurately very feeble radiation, resort has been had to

photography not only to ascertain the extent of the spectrum of the fluorescent light, but also by measurement of the photographed fluorescence spectrum to ascertain the dominant wave-length of the fluorescent colour. This dominant wave-length can be obtained visually by feebly illuminating a pure spectrum colour with white light, and if the visual determination and the photographic determination of the dominant wave-length are identical, we can confidently rely on the exactitude of the photographic measures for the relative brightnesses of the different rays which make up the spectrum of fluorescent light. The study of the luminosity of the different rays is a matter of some importance when considering the theory of fluorescence. I have by me enlarged prints of some plates taken of fluorescence. First of all we have a continuous spectrum of the arc light, then we have a spectrum showing the spectrum of sodium, lithium and magnesium in order to locate the colours of the spectrum, then we have the absorption of the fluorescent body, and next we have a spectrum of the fluorescent light, and finally we have a time scale of gradation of densities. All these exposures being made on the same plate, the development of all the images took place together. The first four images lie vertically one under the other, and the scale number which is attached applies to all of them. These images were all measured at the same places in the attached scale, and the scale of gradation was also measured. The measured opacities of the different parts of the spectra were referred to the gradation curve, and thus the measures were transferred into exposures. Curves of the continuous, the absorption, and the fluorescence spectra were then made from the values obtained from the gradation scale. Finally, the curve of the continuous spectrum was compared with the visual curve of the spectrum of the arc light, and from a comparison of the relative values of the ordinates of the continuous spectrum with that of the fluorescent, the visual curve of the fluorescence light spectrum was obtained. The dominant wave length was calculated by the method which I described in a paper I presented to the Royal Society in 1905. The visual results and photographic results, I may say, are in agreement, showing that in this difficult research photography is to be entirely trusted.

I have, even in the days of wet-plate photography extensively used this method of obtaining quantitative results, and have advocated successfully its employment in astronomical work since the advent of gelatine plates.

I may say that the main point is to obtain a trustworthy scale of gradation—and this must be a time scale of gradation,—that is, one which would be the same if taken on different parts of the plate. Experiments have shown that with carefully-prepared commercial plates there is no need to fear irregularities. In such work as that described, if a second plate of the same fluorescent body gives the same results from measurement, these results may be accepted as correct.

I have not time to enter into the methods adopted of measurement. I can only say that I advocate a method in which both eyes can be used with a minimum of fatigue. Measurements made with one eye only and with optical adjuncts are to me much less accurate than those made with two eyes.

I wish to emphasize to this section the great use that quantitative photography can be to the chemist and the physician.

Etude comparative du Pouvoir Réducteur des principaux Révélateurs organiques et des moyens permettant d'augmenter ou de diminuer avec chacun d'eux les contrastes de l'image développée.

Par MM. A. et L. Lumière et A. Seyewetz.

Les auteurs ont cherché d'une part à préciser les différences que présentent entre eux les révélateurs considérés au point de vue de leur énergie réductrice, afin de déterminer si réellement, comme on le croit généralement, certains développateurs permettent de faire apparaître mieux que d'autres les faibles impressions lumineuses, c'est à dire les détails dans les grandes ombres du sujet photographié.

D'autre part, pour chaque révélateur ils ont étudié et comparé méthodiquement les divers moyens permettant d'augmenter ou de diminuer les contrastes.

Les auteurs sont arrivés aux conclusions suivantes:

Tous les révélateurs quelle que soit leur composition (sauf ceux

qui renferment des produits dissolvant le bromure d'argent) permettent de développer au même degré les faibles impressions des images sous-exposées.

Les contrastes peuvent être modifiés par les procédés suivants :

Diminution des Contrastes.—On peut diminuer les contrastes :

1° En augmentant la dilution du révélateur (3 à 4 volumes d'eau pour 1 volume de révélateur).

2° En additionnant le révélateur de sulfite de soude ou bien en combinant le 1er et le 2me moyen, c'est à dire en diluant le révélateur avec une solution de sulfite à 5 pour cent (3 volumes de solution pour 1 volume de révélateur).

3° En augmentant l'alcalinité du révélateur.

4° En élevant la température du bain de développement.

Le 1er *moyen* s'applique à tous les révélateurs que les auteurs ont expérimentés sauf à *l'hydramine*. Les révélateurs qui sont le moins sensibles à la dilution sont *l'hydroquinone, le métol-hydroquinone, la métoquinone, l'adurol, l'édinol.*

Le 2me *moyen* n'est efficace qu'avec les révélateurs fonctionnant sans alcali, c'est avec le diamidophénol qu'il donne les meilleurs résultats. Il est alors avantageux de *combiner le* 1er *et le* 2me *moyen.*

Le 3me *moyen* est sans effet avec la plupart des révélateurs, il ne donne des résultats intéressants qu'avec les révélateurs suivants : *Acide pyrogallique, métol* et *hydroquinone.*

Enfin le 4me *moyen* ne peut être utilisé pratiquement qu'avec *l'hydroquinone* et *l'adurol*, les autres révélateurs ne donnent par élévation de température qu'une faible diminution des contrastes.

Augmentation des contrastes.—On peut augmenter les contrastes et par suite améliorer les clichés surexposés par les moyens suivants :

1° En diminuant l'alcalinité du révélateur et avec les révélateurs fonctionnant sans alcali en diminuant la quantité de sulfite alcalin.

2° En abaissant la température du bain de développement.

3° Par addition de bromure alcalin.

Les deux premiers moyens ne sont que les corollaires du procédé indiqué pour diminuer les oppositions. La diminution de l'alcalinité peut être obtenue par addition d'un acide ou de bisulfite de soude.

Le 3me *moyen* s'applique à tous les révélateurs, c'est le plus efficace. De très faibles quantités de bromure alcalin suffisent pour produire l'effet maximum. Les révélateurs qui donnent ainsi la plus forte augmentation des contrastes sont les suivants : *acide pyrogallique, hydroquinone, adurol, glycine, iconogène.*

Influenza dell' aggiunta di forti quantità d' Acido Borico sulla conservazione e comportamento del bagno di sviluppo al diamidofenolo.

Pel Professore R. Namias.

Alcuni anni or sono io ebbi ad indicare l' impiego dell' acido borico come ottimo correttivo nei bagni di sviluppo alcalini nei casi di sovraesposizione.

E specialmente trovai efficace l' impiego simultaneo del bromuro e acido borico, cosicchè proposi di preparare una soluzione di bromuro 10% e saturarla di acido borico, tenendo pronta questa soluzione nel laboratorio oscuro per potersene valere nei casi di sovraesposizione.

Molti hanno adottato questa soluzione che chiamai bromo-borica ; fra gli altri mi piace citare il sig. Dilaye che ha trovato l' impiego della soluzione bromo-borica assai efficace anche per lo sviluppo delle prove su carta al bromuro.

Esperimentando più profondamente l' impiego dell' acido borico coi vari rivelatori constatai che l' azione è notevolmente diversa nei bagni che agiscono in presenza d' alcali e nei bagni che agiscono senza alcali (diamidofenolo). Nei bagni alcalini l' acido borico anche da solo esercita una notevole azione ritardatrice sullo sviluppo. Invece il bagno di diamidofenolo, preparato secondo la formula abituale senza bromuro, può anche essere saturato di acido borico. senza che l' azione nello sviluppo si faccia sentire in grado notevole.

La comparsa dell' immagine è appena un po' ritardata, e quasi nullo è l' effetto nei casi di sovraesposizione. Il principale vantaggio ed invero non indifferente è che il bagno di sviluppo al diamidofenolo contenente gr. 50 per litro di acido borico si conserva molto meglio dell' altro sicchè non occorre come l' altro prepararlo al momento dell' uso. Il bagno così preparato ha anche il vantaggio di risentire

in grado minore l' influenza dannosa della temperatura ; perchè ho infatti esperimentato lo sviluppo anche a 25° senza inconvenienti.

È noto che anche il bromuro di potassio ha un' azione ritardatrice assai limitata nei bagni di sviluppo al diamidofenolo, cosicchè anche coll' aggiunta di notevole quantità di bromuro di potassio non si riesce a correggere scarti di qualche entità nel tempo d' esposizione. Fu ciò che indusse appunto a valersi di bisolfito alcalino come aggiunta al bagno di sviluppo al diamidofenolo per rendere possibile la correzione. Ma il bisolfito ha l' inconveniente di diminuire il potere riducente dell' amidolo e basta sorpassare anche di poco un certo limite per arrestare completamente lo sviluppo.

In presenza di bisolfito l' amidolo, che già per sè stesso tende a dare immagini piuttosto deboli, fornisce immagini ancor meno intense cosicchè coll' aggiunta di bisolfito non si fa che ritardare lo sviluppo senza accentuare sensibilmente i contrasti, come hanno provato recentemente anche i signori Lumière e Seyewetz.

E quanto alla conservazione, la piccola quantità di bisolfito che può aggiungersi al bagno di diamidofenolo ha un effetto limitato.

L' aggiunta di acido borico al bagno di diamidofenolo non ha gli inconvenienti del bisolfito ; a qualunque tenore non diminuisce il potere riducente dell' amidolo e conserva il bagno quasi altrettanto bene del bagno con bisolfito, dato il tenore minimo che di questo ultimo si può impiegare.

Per sè stesso pero, come già detto, non ritarda lo sviluppo della immagine che in piccolo grado, ma dà al bagno oltre alla maggior conservazione una caratteristica assai importante, quella di divenire sensibilissimo all' azione del bromuro. Il bagno di diamidofenolo saturo di acido borico, mentre non perde i caratteri dello sviluppo al diamidofenolo acquista due proprietà preziose per la pratica, cioè aumenta alquanto in stabilità e diviene assai sensibile all' azione del bromuro alcalino in modo da permettere di correggere anche forti sovraesposizioni.

Il bagno di cui mi servo è così formato :—

Solfito di soda, crist.	gr. 40
Acido borico, polvere	„ 50
Diamidofenolo (cloridrato)	„ 5
Acqua a formare	1 litro.

A titolo di esempio darò quì i tempi richiesti per lo sviluppo di quattro negative ottenute nelle identiche condizioni.

(1) Sviluppo al diamidofenolo semplice (formula come sopra senza acido borica) .. .. .. 5 a 6 minuti.
(2) *Idem* (con aggiunta di gr. 3 per litro di bromuro di potassio) .. .. 8 a 9 „
(3) Sviluppo al diamidofenolo con acido borico (formula sopra) .. .. 6 a 7 „
(4) *Idem* (con 3 gr. per litro di bromuro di potassio) 17 a 20 „

Come intensità nelle parti più opache dei negativi le quattro immagini si equivalgono, ma per ciò che riguarda i contrasti si ha col bagno (4) un' accentuazione tanto maggiore rispetto agli altri bagni quanto più la posa fu esagerata. Dato il limitato costo del rivelatore diamidofenolo si comprende come la possibilità di impartirgli coll' aggiunta di forti quantità di acido borico, proprietà che sono proprie di revelatori molto più costosi, può costituire in pratica (specialmente per gli stabilimenti ove si producono films cinematografici o edizioni al bromuro) un vantaggio non indifferente.

Soggiungerò che la presenza di molto acido borico nel bagno di sviluppo al diamidofenolo ha anche un vantaggio igienico, diminuendo assai l' effetto irritante che tutti i bagni rivelatori alcalini esercitano sulla cute e che in alcune persone producono non di rado eczemi molto fastidiosi.

Recherches analytiques sur l'altération du Sulfite de Soude en présence de différents révélateurs et d'autres substances qui peuvent entrer dans les bains développateurs.

Par Prof. R. Namias.

L'auteur a expérimenté la stabilité des solutions de sulfite de sodium en présence d'alcalis caustiques, de carbonates, de métabisulfite et de révélateur, des dosages étant effectués quotidiennement sur les solutions librement exposées à l'air en vases ouverts.

L'addition d'alcalis caustiques retarde un peu l'oxydation, tandis que l'addition de carbonates alcalins semble l'accélérer ; l'addition de bisulfite de soude n'a aucun effet pratique en présence d'air en excès.

Si l'on considère non plus une solution de sulfite mais une solution de sulfite de soude et d'hydroquinone, l'altération du sulfite devient plus rapide par addition d'un alcali caustique, plus lente par l'addition de carbonate ou de bisulfite.

L'action réciproque du sulfite et du révélateur tend donc, hors le cas d'emploi d'alcalis caustiques, à ralentir l'oxydation du sulfite en même temps que celle du révélateur.

L'auteur a expérimenté notamment l'hydroquinone, le glycin et le métol ; avec ces révélateurs le sulfite et la substance organique s'oxydent chacun moins vite, lorsqu'ils sont mélangés, que s'ils étaient considérés isolément. La vitesse d'oyxdation du sulfite est indépendante de la vitesse d'action du révélateur, le plus rapide d'entre eux, le métol, et le plus lent, le glycin, ne présentant aucune différence au point de vue de leur comportement vis à vis du sulfite.

Dans certains cas l'oxydation du révélateur précède celle du sulfite ; en d'autres cas ces oxydations sont simultanées.

En ce qui concerne le révélateur au diamidophénol et quelles que soient les additions faites au révélateur (bisulfite ou acide borique) l'oxydation du diamidophénol est toujours complète avant que seulement une troisième du sulfite présent soit oxydé.

Sur les Propriétés révélatrices du Pyramidol.

Par M. L. P. Clerc.

Le Pyramidol, sulfate neutre de la diparaphénylolamine

$$\left\{NH=[C^6\,H^4\,(OH)]^2\right\}^2\,S\,O^4\,H^2$$

est assez soluble dans l'eau froide (1,5%), très soluble à chaud (10% à 100°) ; cette solubilité étant notablement augmentée dans les solutions d'acides ou d'alcalis ; le produit est pratiquement inaltérable à sec ; ses solutions aqueuses pures ou additionnées d'alcalis sont très rapidement altérables ; les solutions acides ou les solutions alcalines additionnées de sulfite sont d'une bonne conservation.

Le Pyramidol révèle en solution aqueuse pure l'image latente, mais fort lentement ; l'addition d'un sulfite neutre accélère la réduction ; l'addition de bisulfite de soude à haute dose ralentit cette réduction, mais ne l'interrompt pas.

Des révélateurs très énergiques peuvent être préparés en ajoutant à la solution sulfitique un alcali caustique ou l'un de leurs succédants habituels ; dans le cas d'emploi des alcalis caustiques, on remarque que lorsque la quantité que l'on en introduit correspond seulement à la libération de la diparaphénylolamine par neutralisation de l'acide sulfurique, le développement est à peine plus rapide et plus énergique que la solution sulfitique neutre du pyramidol. Dès que la dose d'alcali est suffisante pour la saturation des groupements hydroxyles, on obtient un révélateur très énergique, donnant des images très pures, et dont la conservation, même en flacons mi-pleins, est très satisfaisante.

Le solution de Pyramidol dans l'acide acétique très étendue avec addition d'une notable proportion de glycérine constitue un révélateur physique pour papiers à image apparente (P.O.P.) insuffisamment exposés.

Discussion.

M. Balagny : En général, on dit que le brômure de potassium n'a pas d'action sur le révélateur au Diamidophénol : Oui, si on emploie un révélateur normal ainsi composé :

Eau	1,000 gr.
Diamido	5 gr.
Sulfite de soude	30 gr.

Non, si on emploie le sulfite de soude dans une proportion de 1 à

2%. Dans ce cas, une addition de 10 cc. d'une solution de brômure de potassium à 10% dans 100 cc. du révélateur arrête complètement le développement.

Et cette action est encore augmentée par la présence du bisulfite de soude dans le révélateur.

Prof. R. Namias en répondant à M. Balagny dit qu'on ne peut pas absolument comparer l'action du bisulfite avec celle de l'acide borique. En effet, on sait qu'à une certaine limite le bisulfite arrête complètement le développement, tandis que cela n'arrive jamais avec l'acide borique avec lequel on peut saturer la solution révélatrice au diamidophénol et sulfite, sans que dans aucun cas le développement soit arrêté, ni l'action réductrice diminuée. Le bisulfite quand n'arrête pas le développement, réduit toujours plus ou moins le développement.

Herr R. Jahr asked if any comparative experiments had been made of diamidophenol (amidol) developers of *equal* durability made with *boric acid*, and on the other hand with *bisulphites* as to their respective developing powers? *The potash bisulphite was such a powerful preserver* that very little of it was sufficient, and this small quantity would, in *his* opinion, not prevent development any more than an equally well preserving quantity of boric acid could do.

Dr. S. E. Sheppard suggested that a cycle of reactions was involved, by which the oxidising (catalytic) influence of small quantities of ferments—whether organic or metallic oxydases—is inhibited. It is suggested that the oxidation of the sulphite is not accelerated but retarded, but that in any case the state of the solution cannot be determined by chemical analysis, as this inevitably displaces the existing equilibrium.

M. Seyewetz fait observer qu'il a indiqué il y a plusieurs années avec MM. Lumière différentes substances (qu'ils ont appelées antioxydants) qui, ajoutées en très petite quantité aux solutions de sulfite, retardent beaucoup leur oxydation. Ces substances comprennent non seulement les divers révélateurs, mais plusieurs composés organiques réducteurs n'ayant aucune propriété développatrice. Si le sulfite préserve de l'oxydation la substance révélatrice, cette dernière est aussi un antioxydant pour le sulfite.

MM. Lumière et Seyewetz ont cherché à expliquer l'effet de ces antioxydants par l'action d'une diastase qui jouerait le rôle de catalyseur, mais ils n'ont pas pu confirmer cette hypothèse.

M. Seyewetz signale, en outre, à propos des expériences de M. Namias sur la conservation du révélateur au diamidophénol, que les travaux qu'il a publiés à ce sujet avec MM. Lumière relatifs à la faible altération du sulfite du révélateur après l'oxydation complète du Diamidophénol sont entièrement confirmés par les travaux de M. Namias.

Mr. J. Spiller remarked that the discussion of developers had been approached from different points of view and by many well-known workers. One was surprised, however, to hear that a *large* quantity of boric acid was required to be used as a preservative, and then the question arose whether, in the presence of neutral sulphite, there was any different action induced beyond that attaching to a bisulphite, which was regarded as efficient.

Professor Dr. R. Luther sagte: Die verhindernde Wirkung von organischen Stoffen auf die Oxydation von Natriumsulfit ist, wie Dr. Titoff festgestellt hat, eine sekundäre Erscheinung und beruht auf der antagonistischen Wirkung gegenüber der beschleunigenden Wirkung, welche Spuren von Kupfersalzen auf diese Oxydation ausüben. Auch ohne organische Stoffe wird Sulfit nur *sehr* langsam oxydirt, wenn alles Kupfersalz möglichst sorgfältig entfernt ist. Eine Spur ($\frac{1}{100,000}$ Molekulargewicht $CaSO_4$ pro Liter) beschleunigt die Oxydation auf das doppelte.

Herr R. Jahr said: Bisulphite (Potash) introduced by Sir Joseph Swan is a most excellent preservative of developers, especially pyrogallol, one-tenth part of bisulphite being sufficient to preserve a pyro solution for over twelve months' time in well stoppered bottles. This small quantity of bisulphite will neutralise so little of the alkali that the developer is practically not retarded at all by it.

The preserving power of the bisulphite for metol has been stated lately by the speaker and that the results of the experiments appear to be very promising.

Dr. C. E. Kenneth Mees remarked that the reaction of oxidised hydrokinone with sulphite forms dithionate which is the normal product of sulphite oxidation by weak oxidising agents, such as manganese peroxide. Moreover, hydroxides react with quinone to regenerate hydrokinone.

Experiments on the oxidisation of sulphites, like those on the sensitiveness of emulsions, are very likely to be prejudiced by traces of metallic salts, especially iron.

Observations sur les Bains de Virage à l'Or à base de Sulfourées.

Par Prof. R. Namias.

L'auteur avait, dès 1893, indiqué l'emploi des sulfourées à la préparation des bains de virage à l'or. Les communications faites depuis cette époque par divers auteurs et notamment par le Dr. Valenta ont surtout porté sur l'addition d'acides organiques et notamment acides citrique et tartrique.

L'auteur s'est proposé d'étudier comparativement divers autres acides ; il a notamment reconnu le même intérêt aux acides oxalique et lactique, ce dernier étant à préférer si le bain de virage doit être utilisé sitôt après son emploi.

L'allylsulfourée peut être substituée à la sulfourée proprement dite sans qu'en résulte aucune différence.

Tandis que les virages à l'or preparés par addition au chlorure d'or de substances à réaction alcaline (acétates, bicarbonates, etc.) sont, à l'exception du virage au sulfocyanate d'ammonium, assez rapidement détruits, du fait de la précipitation de l'or qui commence sitôt après qu'est terminée la transformation du chlorure aurique en chlorure aureux, les bains de virage aux thio-urées sont d'une stabilité parfaite et peuvent donc être utilisés sans aucune perte d'or et jusqu'à complet épuisement.

Discussion.

M. Balagny dit: Le manque de fermeté dans l'impression photocollographique, le manque d'encre provient presque toujours d'une planche qui a peine à accepter l'encre, parce que *l'insolation par le dos* a été légèrement faite, ou même n'a pas été faite du tout.

On comprend aisément qu'une planche qui est resté hygrométrique ait de la difficulté à absorber le corps gras.

Mais l'insolation par le dos ne peut se comprendre que sur des planches transparentes, telles que les dalles de St. Gobain, dont on se sert habituellement.

Aussi cette raison doit empêcher d'accepter comme support de la couche imprimante, par exemple, une feuille d'aluminium qui est naturellement opaque.

Professeur Namias répondit: En effet, quand on emploie les plaques métalliques, il est évidemment impossible de faire l'exposition par l'envers. Mais aujourd'hui l'exposition par l'envers n'est presque plus employée dans les usines d'impression photocollographique. Il y a d'autre moyen pour assurer une parfaite adhérence de la couche et j'indique, par exemple, celui que j'ai essayé avec un succès constant et qui consiste à ajouter une petite quantité d'albumine au mélange de silicate et bière.

On doit remarquer en outre que l'exposition par l'envers tend à diminuer plus ou moins le contraste de l'image et cela peut réussir fâcheux.

Substitution de composés du Plomb et d'autres métaux à l'Argent des images sur plaques ou films au gélatino-bromure et leur utilisation comme mordants pour la teinture.

Par Prof. R. Namias.

Après avoir rappelé le principe du procédé diachrôme du Dr. Traube par teinture de l'iodure d'argent, l'auteur indique qu'il a expérimenté l'emploi comme mordant du sulfate de plomb, ce sel ayant un pouvoir de mordançage supérieur à celui de l'iodure d'argent.

A cet effet l'image est traitée dans un mélange de ferricyanure de potassium et d'acétate de plomb jusqu'à formation d'un mélange de ferrocyanures de plomb et d'argent ; ce dernier est éliminé dans un bain d'hyposulfite de soude qui, à la concentration de 10 %, ne dissout pas le ferrocyanure de plomb. Ce dernier est transformé en sulfate par immersion dans une solution d'acide sulfurique et de sulfate de sodium. Si l'image est alors plongée dans une solution étendue, à 1 pour 1000 au plus, d'un colorant basique, l'auramine par exemple, le colorant est fixé sur le sulfate de plomb. Après un délai qui varie suivant la nature du colorant et sa concentration, la teinture est terminée et l'on peut procéder au lavage.

L'élimination du sulfate de plomb peut alors s'effectuer par immersion dans une solution saturée d'hyposulfite de soude, mais en l'état actuel de ses expériences, l'auteur n'a encore pu éviter la redissolution simultanée d'une quantité appréciable du colorant.

Discussion.

M. Seyewetz demande à M. Namias, à propos de sa communication sur "Substitution de composés du Plomb et d'autres Métaux à l'Argent des Images," etc., s'il a reconnu que les colorants se fixent sur le sulfate de plomb directement ou bien si la présence d'un colloïde est nécessaire pour la fixation du colorant sur le sel de plomb.

M. Seyewetz a en effet constaté que dans le procédé diachrome du Dr. Traube ce n'est pas l'iodure d'argent lui-même qui fixe la matière colorante mais le gélatino-iodure d'argent. De plus, les combinaisons qui prennent ainsi naissance entre le gélatino-iodure d'argent et le colorant ont des propriétés notablement différentes de celles du colorant lui-même. Ainsi, les matières colorantes basiques du di- et du triphénylméthane telles que le rouge d'acridine, le vert malachite, la fuchsine, le violet cristallisé, etc., qui sont normalement décolorées par le bisulfite de soude, restent inaltérées lorsqu'elles sont fixées sur le gélatino-iodure d'argent, ce qui permet d'employer les solutions de bisulfite de soude pour décolorer instantanément la gélatine sans modifier la couleur fixée sur le gélatino-iodure d'argent. Cette propriété dispense d'un long lavage pour éliminer le colorant qui teint la gélatine.

M. Seyewetz demande à M. Namias s'il a observé les mêmes propriétés pour les colorants basiques fixés sur le sulfate de plomb.

Prof. R. Namias répondit : La communication que j'ai faite a un caractère provisoire ; elle se réfère à des études préliminaires qui me semblent ouvrir un champ assez intéressant d'applications. Je ne puis donc pour cette raison répondre à M. Seyewetz. Je voudrais souhaiter que M. Seyewetz ait à s'occuper de l'argument en y portant la contribution de sa grande science et compétence.

Mr. F. F. Renwick said : I should like to suggest to Prof. Namias the addition to the fixing-bath of hyposulphite of soda, which he uses for removing the lead sulphate, of 10 to 20 % of an alkaline acetate. He will find the rate of fixation greatly increased thereby.

Dr. H. Freundlich fragte : Wurde Herr Seyewetz mir mitteilen ob jede Konzentration der entfärbenden Lösung ausser Stande ist, die gefärbten Bromsilberhörner zu entfärben, oder ob dies nur bei verdünnten Lösungen der Fall ist?

J. Hertzberg read a Paper on

Die Wirkungsweise des Ammonium-Persulfats.

Discussion.

Dr. S. E. Sheppard suggested that the difference in the action of ammonium persulphate was accelerated by the auto-catalytic action of the dissolved silver. Experiments showing the great increase of the oxidising power of persulphate by small additions of $AgNO_3$ had been made by Dr. Marshall of Edinburgh.

Mr. Heathcote said that some experiments carried out eight years ago by himself showed that ammonium persulphate acted *more* slowly, not *faster*, on silver when silver salts (silver nitrate, etc.) were present. On the other hand his experiments revealed the fact that the action of ammonium persulphate was much accelerated by a small rise of temperature. This solution develops more heat on the dark parts of a negative than on the light parts, probably owing to the greater density of the silver particles, and by means of a thermo-couple the difference in temperature between dark and light parts of the same negative in ammonium persulphate solution was measured.

Mr. F. Krohn said low exposures on a dry plate show a coarse deposit close to the surface. Full exposures show a coarse deposit on the surface and a finer deposit lower down near the support. The action of persulphate as suggested by Mr. Friedburg is therefore probably the correct one. Howard Farmer reducer acts by cutting away the deposit on the surface slowly penetrating into the film, consequently the low exposures get reduced or wiped out more rapidly than full exposures.

Professor Dr. R. Luther: Dr. Scheffer hat durch Mikroquerschnitte bereits gezeigt, dass beim Farmer-Abschwächer eine substrative Abschwächung von oben nach innen, beim Persulfatabschwächer eine etwa proportionale Abschwächung (jedes Korn in gleichem Masse) stattfindet. Um die hyperproportionale Abschwächung zu erklären, nehme ich an, dass es eine autokatalytische Reaktion frischer Persulfat und Silber ist: gelöste Silbersalze beschleunigen auch andere Oxydationen durch Persulfat, z. B. die Oxydation von Mangalsalzen.

Photographic Demonstration of Light Absorption.

By L. H. Friedburg, *New York.*

The experiments which are described in the following lines were caused by my desire to reproduce Daguerreotypes as well as common printed matter by direct contact.

In a paper, read before the New York Section of the American Chemical Society, December 9th, 1898, I stated: "It may interest you to hear of experiments performed by myself with a view of practical application. I faced Daguerreotypes to dry plates in a printing frame, and obtained faint but very clearly outlined copies. These copies became more distinct, very likely by contrast, when I exposed the frame to light, the dry plate being thus blackened to the extent of about two inches all around the impression made by the Daguerreotype."

Continuing the experiments and varying them as much as possible, I found that an impression of almost any material which lends itself to such purpose could be obtained upon the dry plate.

The general mode of procedure to which I adhered was the following: A common glass plate, *e.g.*, 8 in. by 10 in., was coated to the extent of 7 in. by $8\frac{1}{2}$ in. with light tight material, thus leaving a clear edge of 1 in. to $1\frac{1}{2}$ in. free all around. The consecutive layers of material for the prevention of access of light were (*a*) black paper, as commonly used for enveloping dry plates, (*b*) red felt, (*c*) very white writing paper. Each layer was fastened upon the edge of the preceding one and overlapping to the glass plate by means of *passe-partout* binding strips. This glass plate was then put into the printing frame, the white paper facing the operator. The substance to be reproduced was placed in the centre of the white paper, and then an 8 in. by 10 in. dry plate followed, the sensitive side in touch with the object and the white paper. The free border of the 8 in. by 10 in. dry plate was then exposed to the action of light, and subsequently developed.

We understand clearly what happened. The light acted freely upon the uncovered part of the dry plate, diffused into it and passed through the remaining covered part of that plate, on to the object, from which it was eventually reflected, so as to arrive a second time at the sensitive surface.

In the beginning of these experiments I endeavoured to make

sure that contact "alone" was not the cause of the action; I therefore duplicated the process, by *not* exposing the frame to light, but leaving it for some time, mounted as before, in the dark. It was further ascertained that here was no case of radiation through the light tight material at work, since no effect was observable when the entire glass plate had been covered with such material, and, everything else remaining as before indicated, the frame was exposed to light. In *both* cases there was no effect produced. Finally, it was proven that no impression was discernible when the whole arrangement of plates was reversed, viz., by putting the dry plate glass-side down into the printing frame, then the object, and then white paper and red felt; the dry plate under this treatment of exposure being, as expected, uniformly blackened on development.

In various experiments I put a mirror behind the dry plate, and also backed it, in other cases, by different coloured paper or glass. But the effect did not seem to be influenced by such variations. In every case a more or less distinct negative or positive was obtained, depending upon the time of exposure.

I did not arrive at any clear conception as to the cause of the effect, which was a striking one, except that the resulting plates were not strong enough, even after intensifying, to allow of good reproduction on paper.

Finally, I sent a short report of the results obtained to Dr. J. M. Eder in Vienna, who referred me to the experiments of Mr. J. Hort Player (see "The Photogram," 1902, page 377), and also to the explanation of the production of Playertypes by Dr. R. A. Reiss in Lausanne (see Jahrbuch der Photographie und Reproduktionstechnik, 1903, page 110). Dr. Eder claimed, that my results belonged to the same class as those of Mr. Player, and that, according to Dr. Reiss, absorption of light by dark surfaces was the cause of the phenomenon.

In order to be sure that my results, which were obtained under different conditions than those of Mr. Player, were essentially of the same nature, I at once proceeded to the test.

I did this mainly, since the Playertypes are produced by copying a negative in such a manner as to put "printing-out paper" into the path of the light upon the negative, while I, in doing the same (in one case, see above) with a dry plate, had not obtained a similar result.

The experiments which I performed in corroboration of Dr. Reiss' explanation were the following:—

(1). It seemed clear that if absorption is the cause of the phenomenon in question, that *any* kind of absorption should produce the effect. Consequently I chose as the absorbing surface an unused small (4 in. by 5 in.) dry plate. This one I placed on the middle part of the white paper with the sensitive side upwards. Upon it was put a small strip of writing paper with a few words of print on it, and showing the written words "dry plate." Then the large 8 in. by 10 in. dry plate was put with its sensitive side against the small one, and, after covering it with red felt, the printing frame was closed and exposed for a few seconds to subdued daylight. The developed and fixed negative which resulted showed a densely black border, gradually passing over into a zone of perfectly clear glass, and in the centre a sharply defined black square showing the printed and written letters, also in clearness of glass. However, on closer examination it was seen that these letters were not as clear as the square; there was a shade of grey in them. The dry plate had therefore absorbed light in a greater measure than the written and printed letters.

(2). The conditions in this experiment were the same as in (1), but as an object I used a 5 in. by 7 in. glass plate which was coated with phosphorescent paint, and which had been kept entirely dark for a very long period. The resulting negative showed again a deep black border, and a true copy of the luminous-paint plate, showing all the detail of the lines of the brush; the copy of the paper-square was less black than that of the paint plate, and again the written letters were glass-clear, as before. The luminous-paint plate had not absorbed any photochemical rays, or if so, not enough to prevent reflection.

(3 and 4). In these experiments also the same order of arrangement was adhered to. The object used for reproduction was an old, unused Daguerreotype plate, which was highly polished. The white paper square showing print and writing was omitted. Two results were obtained. In the first, a densely black border and a glass-clear reproduction of the silver plate resulted. In the second, which was intentionally overexposed, the border was positive, showing clear glass and the silver plate appeared in deep black. We must conclude that in the first case the time of exposure had been too short.

(5). Table VIII., Farbentafel of Dr. H. W. Vogel's "Handbuch der Photographie, Berlin, 1891," was used as an object. This plate shows nine coloured squares and beneath them the nine photographic impressions which these colours produced upon an ordinary dry-plate.

This object offered a good opportunity to see whether the absorption brought about by our process is the same as that produced by reflected light in the ordinary manner of photographing. The result showed this to be a fact, since no marked difference could be noticed between the resulting negative and that from which the reproduction on the "Farbentafel" had been obtained.

There seems to be no doubt possible as to how the effect described in the above experiments is brought about, and that Dr. Reiss' explanation is to be considered as the correct one. If anything could be added, it is this, that not only the absorption of light by dark surfaces can be photographically shown in the manner described above, but any absorption whatsoever of light can be suitably demonstrated thus.

Ueber die latenten Bilder der Röntgenstrahlen und anderer Energiearten.

Von Dr. Lüppo-Cramer, *Frankfurt a/M.* (*in Vertretung des nicht anwesenden Autors vorgelegt und mit Demonstrationen begleitet von Herrn Chapman Jones*).

Der latente Eindruck, den die Röntgenstrahlen und Radiumstrahlen auf die photographische Platte ausüben, verhält sich insofern analog dem latenten Lichtbilde, als in beiden Fällen unter Abspaltung von Brom sich Keime von Silber bilden, an denen sich bei der Entwicklung weiteres Silber anlagert. Dies beweist die Tatsache, dass man die latenten Bilder auch jener Energiearten zuerst fixiren und dann entwickeln kann.

Neben dieser chemischen Veränderung des Bromsilbers üben aber die Röntgenstrahlen und Radiumstrahlen, sowie auch ultraviolettes Licht und intermittirendes längerwelliges Licht eine Wirkung auf das Bromsilber aus, die ich auf Grund eingehender Versuche als eine *Zerstäubung* gedeutet habe. Näheres hierüber, sowie über die Literatur dieses Gebietes findet man in meinem soeben erschienenen Buche "Die Röntgenographie in ihrem photographischen Teile" (Knapp.—Halle).

Jene latenten Bilder (auf Schleussner Diapositivplatten) treten ohne Anwendung eines Entwicklers oder überhaupt irgend welcher

chemischer Agenzien im Tageslichte sofort in die Erscheinung. Dabei färben sich die von den X-Strahlen getroffenen Teile der Platte intensiv rot, die nur vom Lichte getroffenen bläulich-grün. (Demonstration solcher Platten und "Entwicklung" derselben durch Licht.)

Latente Lichtbilder auf Daguerreotyp-Platten lassen sich, wie schon Becquerel 1840 beschrieben hat, durch Licht entwickeln, nicht aber durch weisses oder blau-violettes Licht, sondern nur durch langwellige Strahlen (rot und gelb). Ich habe gefunden, dass dieses in der photographischen Literatur ganz vergessene, teilweise auch wohl gar nicht geglaubte Experiment auch auf Jodsilbergelatine-Platten sehr gut gelingt. Das unsichtbare Bild auf Jodsilbergelatine tritt bei der Belichtung ins Tageslicht unter einem gelben oder roten Glase in wenigen Minuten hervor, die "Rayons continuateurs" (nach Becquerel) setzen die von den kurzwelligen Lichtstrahlen ("Rayons excitateurs") begonnene Arbeit fort. (Demonstration eines Bildes auf Jodsilbergelatine, das durch gelbes Licht ohne Anwendung eines Entwicklers hervorgerufen war.)

Angeregt durch eine kürzlich von Idzerda in Delft auf Grund meiner Arbeiten ausgesprochene Vermutung, dass vielleicht auch die X-Strahlen ihre eigenartige Wirkung als "Rayons excitateurs" im Sinne Becquerels ausüben könnten, habe ich versucht, ob man nicht auch die Röntgenstrahlen durch Nachbestrahlung mit rotem Lichte verstärken könne. Dies ist in der Tat möglich, allerdings, soweit meine Versuche bisher ergeben haben, wieder nur bei Diapositivplatten. Die mit X-Strahlen in gewöhnlicher Weise vorbestrahlte Schleussner Diapositivplatte erlangt (bei nachfolgender gewöhnlicher Entwicklung) eine mindestens dreimal so hohe "Empfindlichkeit," wenn man die Platte vor der Entwicklung 5-10 Minuten unter einer roten ("Massiv-Rubinglas") Scheibe dem Tageslichte aussetzt.

Wie schon Villard 1899 gefunden hat, werden bestimmte Sorten gewöhnlicher hochempfindlicher Trockenplatten durch Vorbestrahlung mit Röntgenstrahlen bis ins Ultrarot "optisch sensibilisirt." Dieses interessante Phänomen, das, wie leicht ersichtlich, auf demselben Princip beruht wie die vorher besprochene "Verstärkung" des latenten Röntgenstrahlenbildes auf Diapositivplatten durch Nachbestrahlung mit rotem Lichte, tritt bei hochempfindlichen Platten erst im Gebiete der Solarisation zu Tage. (Demonstration einer Kopie: Duplikat-Negativ.)

Die von mir als Zerstäubung gedeutete eigenartige Veränderung

Optische Sensibilisierung durch Röntgenstrahlen. Negativ.

des Bromsilbers durch Röntgentstrahlen und verwandte Energiearten ist in weitgehendem Masse von der rein chemischen Veränderung (Halogenabspaltung) unabhängig. Man kann, wie schon aus Villards Versuchen hervorgeht, das latente Röntgenstrahlenbild minutenlang dem vollen Tageslichte aussetzen, ohne dass das Bild seine Entwickelbarkeit verlöre. Auch eine vorherige Bestrahlung mit Tageslicht verhindert nicht die Aufnahmefähigkeit der Platte für ein latentes Röntgenstrahlenbild. Auch Radiumstrahlen und Funkenlicht verhalten sich ebenso.

Von weiteren Phänomenen, die für die Kenntniss der Natur des latenten Lichtbildes von grosser Bedeutung sind, möchte ich dem Kongresse das interessante Verhalten der Photobromidgelatine demonstrieren. Das rote Photobromid, d.h. mit kolloidem Silber "angefärbtes" Bromsilber, wird durch Belichtung nicht dunkler, sondern vielmehr zu hellgrauweisser Farbe ausgebleicht. Im Entwickler wird das unbelichtete Photobromid geschwärzt, das belichtete dagegen bleibt unverändert. Wir erhalten also bei der Aufnahme keine Negative, sondern direkte Positive. (Demonstration solcher Platten.) Bezüglich der theoretischen Erklärung dieser neuartigen Vorgänge verweise ich auf meine demnächst erscheinenden Publikationen in der "Photographischen Korrespondenz."

Discussion.

Herr John Hertzberg sagte: Eine gewöhnliche Bromsilberplatte wurde nach vorherigem Boden in Fluoresceinlösung im Lichte exponiert. Ich sagte mir: Wenn bei der Beleuchtung Brom frei werden könnte, würde es sich vielleicht mit dem vorhandenen Fluorescein zu Tetrabromfluorescein (Easin) vereinen, dass durch seine intensieve Farbe, wenn auch Spurenweise vorhanden, zum Vorschein kommen könnte.

Versuche haben gezeigt, dass bei kurzer Beleuchtung keine Färbung zu bemerken war, nach Beleuchtung während einigen Minuten beim Tageslichte hat sich die Platte violettgrau gefärbt, nach dem Fixieren zeigte sich auf den exponierten Stellen eine sehr schwache gelbrote Färbung.

A Paper was read on

The Reversal of the Photographic Image.

By Wilder D. Bancroft.

Différents effets des sensibilisateurs sur les Plaques sensibles selon les propriétés du Bromure d'Argent de l'émulsion.

Par S. de Prokoudine-Gorsky.

---

1. Le bromure d'argent de chaque marque de plaques photographiques possède des qualités individuelles qui lui sont propres, sous le rapport de la sensibilité aux rayons du spectre, et cela indépendamment de la constitution de l'agent sensibilisateur.

2. Le panchromatisme n'appartient qu'aux plaques photographiques dont l'émulsion fournit, sans sensibilisation préalable, un spectrogramme à tendance bien caractérisée à se laisser impressionner, ne fût-ce que dans une faible mesure, par toutes les parties du spectre.

3. Pour obtenir, dans un but spécial, une haute sensibilité aux rayons d'une partie définie du spectre, il est nécessaire d'opérer la sensibilisation, de préférence, sur les plaques qui, avant leur sensibilisation, possèdent une sensibilité particulièrement prononcée pour cette section du spectre, même si le degré de sensibilité générale de cette marque de plaques ne satisfait pas aux exigences courantes.

4. Les conclusions basées sur la mesure du degré de sensibilité des plaques au gélatino-bromure d'argent sont sujettes à caution, à moins qu'elles ne soient corroborées par le spectrogramme de la plaque non sensibilisée (la courbe du spectrogramme, à elle seule, est insuffisante).

5. La comparaison entre elles des échelles des différents systèmes de sensitomètres basée sur des sources de lumière différentes est non seulement peu scientifique, mais est une source inévitable d'erreur. Toute comparaison de ce genre doit donc être absolument proscrite.

Discussion.

M. L. P. Clerc dit : L'existence de la sensibilité initiale du bromure d'argent aux radiations les moins réfrangibles a déjà été mise en évidence, notamment par le Dr. Precht, qui a montré que la teinture par colorants ne crée pas la sensibilité chromatique, mais a pour seul effet de l'exalter considérablement.

Il est regrettable que l'auteur n'ait pas précisé plus complètement les conditions de ses expériences spectrographiques et qu'il n'ait pas indiqué notamment s'il a travaillé avec un spectre de réseau ou avec un spectre de prisme.

La non-comparabilité des résultats sensitométriques fournis par des sources de lumière différentes a été mise en évidence par tous les Congrès de Photographie antérieurs et n'est donc plus discutable actuellement. Il en est de même relativement à la non-conformité des résultats fournis par le sensitomètre Warnerke non seulement avec les autres sensitomètres, mais aussi avec lui-même—de nombreux modèles de ce sensitomètre permettant l'obtention de teintes assez intenses, en l'absence même de l'écran phosphorescent, et ceci grâce à la translucidité du volet de l'appareil.

Dr. C. E. Kenneth Mees said : Sensitising is a question of the manufacture of the emulsion. The fluoresceins require ammonia emulsions, the isocyanines boiled emulsions. It seems to be doubtful whether sensitising can be connected with the previous colour-sensitiveness of the plate.

Herr R. Jahr said : Collodion emulsion is more easily colour-sensitised than bromide plates, but has no greater initial sensitiveness to yellow, orange, and red. The demand of the author of the paper for standardising every particular batch of plates will hardly be fulfilled. Who would like to pay for such plates ? The Lippmann plates, prepared according to the formulæ of Dr. Lehmann, of Zeiss, Jena, by the speaker, show, in the Chapman-Jones sensitometer, a rather strong deposit in the red before the blue square shows any action at all.

Photo-Chemical Deterioration of Oil Paintings.

By Maximilian Toch.

All oil paintings show an unmistakable sign of age, and students who visit the various art galleries and copy old oil paintings invariably gloss them with a lake colour or asphaltum, so that the lighter colours are toned down and show a yellowish brown tinge, which to all of us indicates the signs of age. There is nothing written in the entire literature of oil painting, as far as the writer could learn, which gives a proof of the cause of this deterioration, but a number of writers have all suggested a certain remedy, which, to a large extent, amounts to the same thing: such as the exposure of a painting to bright sunlight. The change in colour is always more apparent in the high lights, and where light tints have been used, and inasmuch as water colours, pastels, and tempera painting do not show this particular deterioration, it is quite evident that the cause does not lie in the pigment itself, nor in the sub-stratum upon which it is painted, but in the medium which is used to bind the pigment to its foundation. In searching for the cause, an analogous condition exists on walls of buildings which are painted in oil paint, for it is always apparent that where the sun shines on a wall it either retains its pristine colour or becomes more brilliant, and back of a picture there is a distinct yellowing or browning of the pigment which shows equally a line of demarcation where the picture hung. Similarly again is the evidence that no such yellowing occurs where walls are painted with distemper or water colours, but in every instance is this particular reaction apparent where oil pigments are used. In finding the cause, it is more or less simple to find a remedy, and a series of experiments were tried by the author in the following sequence, and with the following results.

That the cause was due to what may be termed the effect of light on a mixture of white lead, zinc oxide, and linseed oil, or a linseed oil varnish, is absolutely apparent, for paint chemists have known that white lead in any form, whether it be called flake white, Kremitz white, silver white, or white lead, has a reducing action on the pigment contained in linseed oil, or linseed oil varnish, and this reducing action changes this pigment contained in linseed oil into another pigment which is yellow. It may fairly be asked that such

cannot be the case if the linseed oil be bleached, but to this the reply must be given that the bleaching of linseed oil does not destroy the colour which is in it, but simply changes it from an olive yellow to an exceedingly pale yellow, which is not apparent, so if we take refined or bleached linseed oil and mix it with white lead or a pigment containing white lead or zinc oxide, we have a very brilliant white which remains white as long as it is exposed to bright light. If we take this mixture and place it for six weeks in an absolutely dark place, the white paint changes into a well known yellow, and it is this particular change which produces in all paintings the distinct yellowness of age. Flax seed, from which linseed oil is made, contains a colouring matter which is known as chlorophyll, and is the same colouring matter which is found in all plants in many of the woods and in a large number of gums and resins, particularly in the fossil resins.

Vibert, the well known French painter, knew this fact without having been able to trace it to its chemical cause, and this led him to abandon all linseed oil as a binding medium and substitute petroleum and colophony compounds with which he painted most of his pictures. Nearly all of his subjects contain little or no light colours, such as whites or straw colours, but as his particular forte lay in painting pictures of cardinals, the original brilliancy of his paintings still maintains, and there is no reason why his pictures should not endure for centuries, if they are properly protected from any influence of the elements and obnoxious gases of modern civilisation. A large series of experiments were therefore made, and the colouring matter of flax seed, grass, and the fossil resins were taken and mixed with white lead and zinc oxide (zinc white), exposed to the sunlight for a short time and then placed away in a dark closet for varying periods from six weeks to three months. In every instance the white turned yellow: sometimes a bright canary yellow, sometimes a dirty yellowish brown, but always the yellow effect was obtained. A similar line of experiments were made in which gum damar was dissolved in turpentine, naphtha, and benzole, and the results carefully noted. Gum damar and turpentine showed only an exceedingly slight decomposition, and gum damar containing a small percentage of benzole and a large percentage of naphtha showed no decomposition. The human eye is not very sensitive to these shades, but fortunately we have the photographic plate, and a photograph taken of these various mixtures on plates which are not over sensi-

tive to yellow show up these results with better effect than the human eye can discern them in the original chlorophyll experiment. Another line of experiments were tried in which bleached linseed oil was taken, and this turned exceedingly yellow in three months, but when exposed for three months to the bright sunlight it became brilliant white again, and upon being placed in a dark closet for another three months no change took place, for those parts of the painted experiment which had been bleached by the sunlight remained white in the dark closet at the end of the experiment. This would, therefore, prove that when a picture has turned yellow it can safely be exposed to the sunlight in order to bring it back to its natural brilliancy, provided, of course, that no part of it has been painted with asphaltum or bitumen, for the asphaltum and bitumen, instead of bleaching in the light, become black. To those who are interested in this photo-chemical experiment, the author refers to his paper on "The Influence of Sunlight on Paints and Varnishes," reprinted from the Journal of the Society of Chemical Industry, April 15th, 1908, No. 7, Vol. XXVII.

Nearly all of the varnishes, with few exceptions, aid largely in this deterioration of oil paintings, for the reason that the colouring matter in a dark place or away from the brilliant light changes from a neutral or unseen tint to a yellowish tint, which is a direct decomposition of chlorophyll into one of its lower bodies, and a similar line of experiments were conducted, and wherever such resins be used like Manila copal, West Coast copal, or Zanzibar copal, they all turned yellow, even though no linseed oil was present, and it is, therefore, easy to conclude that these and all fossil resins contained some colouring matter that grass, flax seed, or, in some instances, turpentine, may possess. Furthermore, all of these fossil resins when used for making varnish are reduced or fluxed in a solution of linseed oil. The varnishes which, however, do not show this same effect are the alcohol varnishes composed of solutions of bleached shellac, sandrac, and mastic ; however, showing some slight tendency toward turning yellow. The one resin which, however, resisted the action of darkening when mixed with white lead was gum damar. As there are three well known varieties used in the arts, the author has found that Batavia, Singapore, and Pedang, when selected for brilliancy of colour in their original state, are the safest to use, but there are varieties of these three gums which are originally yellow, and should be avoided either as a varnish or

a medium for oil painting. Some criticism may be urged that the solution of gum damar is not sufficiently binding as compared with linseed oil, but to this the answer must be made that an oil painting is never exposed to the elements and is certainly more tenacious and less liable to decomposition than the media used by the ancients: such as white of egg, mucilaginous matter, etc., and we naturally have records where paintings have lasted for upwards of twenty centuries painted by the Romans with poor and weak media. Of the solid white pigments, which superinduce the decomposition of oil and varnishes, white lead is the strongest in its action, and zinc sulphide, or lithopone, is the weakest. It has been urged that lithophone, which is a mixture of zinc sulphide and barium sulphate —barium sulphate being the old permanent white or blanc fixe— should be substituted for all white pigments in oil painting, but this cannot be urged at present for the reason that the majority of the lithopones are acted upon by light and turn grey, although there are a variety of patents for the manufacture of lithopone which are alleged to be permanent. On looking into these we find that their brilliancy is superinduced by the addition of a soluble salt such as nitrite of soda, and when lithopone, either according to the special American patents or to the German patents, be mixed with gum damar solution no change takes place, but when mixed with linseed oil, either bleached or unbleached, the soluble salt has the same effect which white lead possesses in so far that it reduces the colouring matter from a neutral and unseen tint to a yellow or yellowish pigment, and, therefore, no advantage is gained at present by the use of this so-called permanent lithopone. Zinc oxide, or zinc white, is therefore still the most permanent, although permanent white or blanc fixe has absolutely no effect, but it has the inherent weakness in so far that it has no hiding power and is really more of a glaze than an opaque pigment. If linseed oil is, however, insisted upon by the painter the raw unbleached unrefined product should be used, for it is reasonable to assume that it cannot grow any darker as long as the colouring matter is not visibly hidden, but may improve, for upon exposure the colouring matter will surely bleach, and upon replacing in a poorly lighted room it will not grow any darker than it originally was when the painter used it. Some painters use poppy oil, which is almost colourless; other painters use walnut oil, but the author finds that while poppy oil and walnut oil are not so prone to become yellow with age, they nevertheless do

become yellow and have, in addition, the faculty of drying exceedingly slow, which interferes largely with the progress of the painting. The driers that painters use are also to be avoided. The one colour, megilp, which contains both lead and manganese, frequently exhibits a dirty pink, and the sugar of lead drier turns the oil yellow even quicker than white lead does.

Summing up the facts before us, it is reasonable to conclude that, in order to make a painting permanent, a medium like damar varnish, which has back of it a long history, and is not experimental, may be advocated for general use as a varnish with which to glaze a painting and preserve its permanency, which has very few defects and much in its favour. In looking over the works of the Flemish artists, particularly those by the Van Eycks, which may be seen in the London galleries, it is quite evident that all these painters used a medium other than tempera. It is exceedingly likely that the medium contained some linseed oil, and possibly a varnish composed of an easily soluble gum, either like damar or mastic.

Abstract of the Report on the present Condition of Sensitometry.

By C. E. Kenneth Mees, D.Sc.

The subject of sensitometry is made more difficult by the scattered nature of the literature referring to it, no book on the subject existing, and special authors dealing mainly with their own methods. The object of this report is to compare the various methods which are in actual use. The subject may be divided into four branches:—

(1) The measurement of the sensitiveness of plates.

(2) The measurement of the rate of development of plates.

(3) The measurement of the colour-sensitiveness of plates.

(4) The application of plates to the measurement of phenomena.

The first division, or sensitometry proper, as it may be termed, is the attempt to find a number which shall accurately represent the relative sensitiveness of two different plates. Since different plates will vary under different conditions, no such absolute number can be given, but a satisfactory definition will be the ratio of the exposures required to produce equal densities, when the two plates are developed to equal gradations; the light source employed being daylight, and the exposure being not less than five seconds nor more than two minutes.

The methods which have been employed are, intensity scale sensitometers of the Warnerke type, and time scale as in the Scheiner wheel, in both these methods the lowest light intensity producing effect being measured; the methods of the Congress of Photography, and of Sir William Abney, and finally the method introduced by Hurter and Driffield, where the sensitiveness is read from a curve connecting the density of the developed plate with the logarithmic exposures received. The second part of sensitometry consists of the determination of the law of development, and of constants peculiar to each plate. Colour sensitometry may be performed by measurements of the density of a plate which has been exposed to the spectrum, or by finding the ratios of sensitiveness under sets of coloured filters. If the sensitiveness and development constants of a plate are known, then that plate can be used for the measurement of intensities, either of light or of radio-active phenomena.

Discussion.

Mr. F. F. Renwick.—I have a good deal of work on this subject almost ready for publication, and if the members will allow me to give them a brief summary of some of the more important results, it will, I think, add to the interest of the discussion. Shortly after the publication of Sheppard and Mees papers, I set up a very similar exposing apparatus to theirs and started work with it. The irregularities and uncertainty of the results very soon involved me and my late colleague, Mr. Potter, in a lengthy study of the causes of these anomalies of which I will mention only those that have been established by concordant repeated observations to my full satisfaction.

I. *Local variations in the acetylene flame.*—I find that an acetylene flame is by no means uniform in brightness over the white area. A Bray's Elta burner was selected from among those on the market as giving the flattest flame and showing least tendency to choke, and it was found that the area of uniform brightness in the centre line of the flame was not more than $\frac{1}{8}$ inch in height, the flame itself being about 1 inch high. On the lower side of this area and within $\frac{1}{8}$ inch of it the brightness falls off very rapidly towards the dark area of the flame; on the upper side it falls off more gradually for about another $\frac{3}{16}$ inch and then rapidly again. It is therefore of the utmost importance to locate this uniform area and to use a screen with a small aperture close to the flame for isolating it.

II. *Difficulty of determining the value of this secondary standard in terms of a primary standard.*—The Hefner Amyl Acetate lamp was taken as primary standard.

I find that the value obtained for the secondary acetylene standard, which value of course affects equally all subsequent speed determinations, varied enormously according to the plate used for effecting the comparison thus:—

Plate used.	Value of Acetylene Secondary Standard.
Ilford Ordinary	$91\frac{3}{4}$ HK. M. S. per min.
Imperial ,, ...	96 ,, ,,
Wratten ,, ...	$103\frac{1}{2}$,, ,,
Seed Gilt Edge	$70\frac{1}{2}$,, ,,
Royal Standard (Rapid)	66 ,, ,,

These results were proved to be largely due to differences in the curves of colour sensitiveness of different brands of plates.

Thus Ilford Empress and Special Rapid have practically no sensitiveness beyond the blue green towards the red end of the spectrum, while Ilford Zenith and X Ray are notably sensitive to red and slightly to spectrum yellow and green, and these differences are equally true of other makers' plates.

The above results are, however, not entirely due to differences of colour sensitiveness, but are complicated by still another source of error directly attributable to the use of the well known sector-wheel for giving the required range of exposures.

In searching for an explanation of some of the anomalous results obtained, the effect of varying the total exposure behind the sector wheel was examined, with the result that the inertia value obtained was found to depend on this exposure to a large extent, especially with very slow plates.

The following will serve as an illustration. Plate 2,575:—

Total exposure through 180° arc of Sector Wheel.	Value of 'i' found.
60 HK. M. S.	0·72 HK. M. S.
120 ,, ...	0·795 ,,
360 ,, ...	0·91 ,,

Plate 450:—

Total exposure through 180° arc of Sector Wheel.	Value of 'i' found.
120 HK. M. S.	2·72 HK. M. S.
360 ,, ...	3·64 ,,

Not only is the actual value obtained dependent on the exposure, but the *relative* speed value for two simultaneously exposed plates is also largely dependent on exposure when there is a fair difference in speed between them.

Two plates A and B gave a relative speed value $\frac{A}{B} = 3{\cdot}42 : 1$ for 120 HK. M. S. total exposure and $3{\cdot}93 : 1$ for a total exposure of 360 HK. M. S.

These results are, of course, due to the intermittent character of the illumination and the failure of dry plates to correctly sum up the numerous short exposures received.

In face of these results and some points which I have not yet had time to clear up, it seems to me that in spite of the considerable amount of useful work that has been done on the subject, accurate sensitometry must still be looked upon as in a very unsatisfactory

position, and much work on fundamental matters still remains to be done.

Sir W. Abney said:—I was very glad to hear Mr. Renwick's figures about the uncertainty of the results when exposures were made through the sectors. Ever since the days of Hurter and Driffield I have called attention to the research I made on intermittent exposure. I showed that with slow plates, at all events, the densities obtained by the exposures through the sectors did not nearly agree with the exposures made by exposing in time. Astronomers have recognised these researches, but photographers have not taken notice of them as a rule.

Mr. Chapman Jones remarked:—Sir W. Abney will agree that the relation between the densities as determined when the scattered light is lost or chiefly lost, as in Hurter and Driffield's original method and many modern instruments, and when the whole of the light transmitted is measured, is a variable quantity. By bleaching the deposit the proportion will be very radically altered.

As to the maximum possible sensitiveness, which the speaker understood Dr. Mees to put at about 350 H. and D., the speaker once received from Mr. Cadett plates that registered 400 H. and D., but they proved unstable.

Dr. Sheppard, alluding to the question of intermittent exposure, stated that the effect of this was greatly intensified if a slight quantity of a desensitiser be present, an always possible component in emulsions, especially slow ones. Hence the speaker supported the proposal that the *standard method of exposure* be by a continuous-time scale, such as might be obtained by a band driven by a chronograph.

Herr R. Jahr made a proposal as to sensitometry, etc., at future Congresses:—That papers to be read at a Congress be prepared and distributed beforehand, so that a really useful discussion might result. Scientists, amateur and professional photographers, as well as plate makers, should be invited to take part in this discussion.

An International Standard Method of Marking the Speed of Photographic Dry Plates, and Definitions of the Standard Conditions under which such Speed Tests are to be carried out.

By F. W. T. Krohn.

Anybody who has had much to do with the manufacture of dry plates must long ago have come to the conclusion that the Hürter and Driffield method for determining the characteristic curves of a plate is the one which places in his hands, if not the best, at least the most "practically useful" method for studying the peculiarities of his emulsions. I take it, therefore, that few will deny that this method holds and will continue to hold the field in the study of emulsions, for it can do for the emulsion maker what the balance does for the chemist.

I have, however, been convinced for many years now, that the way in which the method is applied to the speed determination of plates, suffers largely from the defect that users of the method are not agreed about certain essentials, *i.e.*, certain standards and standard methods of working, and that until such agreement can be arrived at the method and the studies to which it is applied are shorn of much of their usefulness. Till now every man has been a law unto himself and has used the light he thought best, the exposure machine he thought best, the photometer he thought best, the developer he thought best, and so on. If I choose, I can with perfect truthfulness, mark the speed of a film H. and D. 180 or H. and D. 100. In the first case I simply record the speed as taken at a development factor of $\gamma = 1$, the readings having been taken with a Koenig Marten photometer. In the second case I record the speed as taken at $\gamma = 2{\cdot}4$, the readings having been taken with a Hürter and Driffield photometer fitted with a Schmidt and Haensch eye-piece.

Again, take two films A and B. Tested with the ten candle pentane standard, we get the speeds as $\begin{matrix} A = 75{\cdot}5 \text{ H. \& D.} \\ B = 131 \text{ H. \& D.} \end{matrix}$ Tested with magnesium light we get the following speeds under otherwise the same conditions $\begin{matrix} A = 142 \text{ H. \& D} \\ B = 121 \text{ H. \& D} \end{matrix}$. The reason is obvious, and to daylight, in the camera, the latter speeds are found to be correct.

I fully recognise that fortunately for dry-plate manufacturers,

plates as ordinarily manufactured possess a considerable degree of latitude, and fortunately the average user of a plate merely asks for data which will enable him, with reasonable certainty, to determine the exposures he must give to a plate in order to obtain a negative which will not take too long to print and which will give him a print on gelatino-chloride P.O.P. that shall be reasonably satisfactory to the eye. Provided he got this last result, the average user would not mind if the speed numbers on boxes laid no claim to absolute accuracy as they apparently now do, but were marked according to a method which would be recognised as merely approximate or conventional, say as follows:—

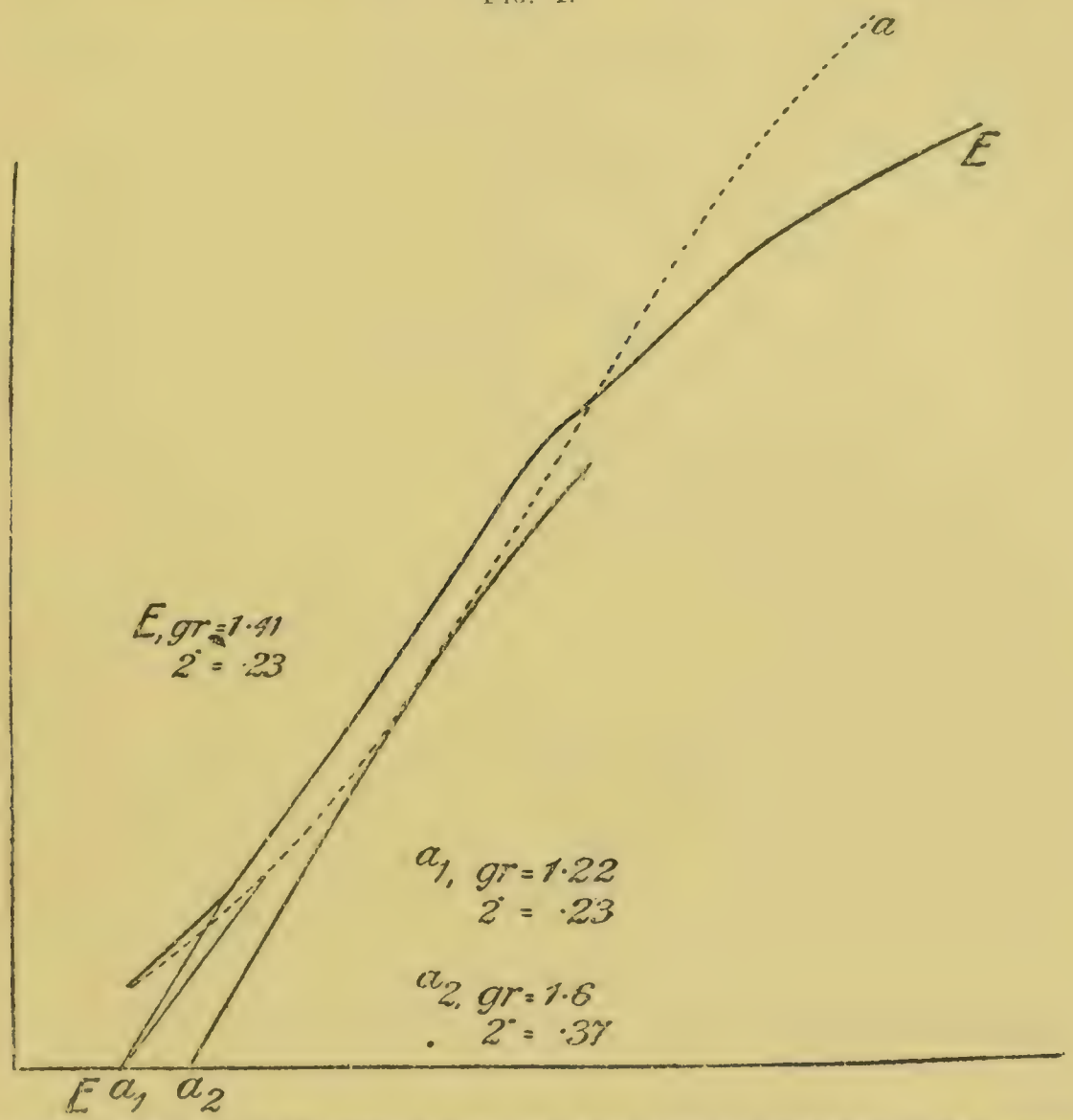
"Slow" ...	H. & D. / 2·5X,	meaning	approximately	25 H. & D.	standard	speed
"Medium" ...	H. & D. / 5X,	„	„	50 H. & D.	„	„
"Rapid" ...	H. & D. / 10X,	„	„	100 H. & D.	„	„
"Extra Rapid"	H. & D. / 20X,	„	„	200 H. & D.	„	„
"Lightning"	H. & D. / 40X,	„	„	400 H. & D.	„	„

with a $\pm 33\frac{1}{3}$ per cent. margin implied in each case.

Once a standard H. and D. speed is defined, the manufacturer will, with the above apparently loose method of marking, be able to give his average customers as useful information in a nutshell, as if he gave them the actual standard H. and D. speed or speeds. These latter could, of course, be marked separately on the boxes as "standard H. and D. speeds." In some cases the information would be more useful. Take, for instance, the following case. H. and D. define a perfect negative as a negative in which the opacity logs (or densities as they are less correctly called) of the silver deposits in different parts of the plate are proportional to the logs of the exposures to which those different parts of the plate have been subjected. The characteristic curves of the plate enable us to determine the correct exposures necessary for obtaining a perfect negative, under any circumstances. But here is a case which at once shows that the theoretically correct speed of a plate is not necessarily the practically useful speed; in fact, this is one of the cases which may have to be taken into consideration when the definitions of "standard H. and D. speed" are set up (see fig. 1). Curve A has such a long period of under-exposure, that it can be said to almost show two speeds or two periods of correct exposure. To be strictly accurate the manufacturers would have to mark the speed as 92 H. and D. Curve E shows a different but more normal type of curve, and the speed would have to be marked 148 H. and D. Yet, on making exposures in the camera under the same

conditions and timing the exposure for the E curve, one gets two negatives which are almost undistinguishable to the eye. How is a manufacturer to deal with such a case? If allowed to give the "conventional speed," he would make both films "Extra Rapid" H.

Fig. 1.



and D./20X, and the results obtained with both films would be almost identical, whereas if he marked the films correctly $\begin{matrix}\text{A} = \text{H. \& D. } 92 \\ \text{E} = \text{H. \& D. } 148\end{matrix}$ he would obtain a more correct, but unnecessarily opaque negative with the A film.

For practical and commercial purposes then, it seems to me that it will be advisable to recognise that a "conventional" or "practically useful" method should be allowed, based on the "standard speed."

And now to the question of "standard speed." From the point of view of research the uncertainty which has existed up till now (where each man as it were measures lengths in feet by the length of

his own feet), has been all to the good, for this uncertainty has incited to research. But surely for the purposes of accurate work it is time now that the standard conditions for speed testing should be defined. Once we have the standard conditions defined and once we agree as to what is meant by the "standard H. and D. speed" of a dry plate I believe an accuracy of ± 5 per cent. will be possible, which is almost scientific compared with the accuracies (I could better call them inaccuracies) such as I have already mentioned above.

In determining and defining the "standard speed" of a dry-plate or film, the following are some of the points which will have to be taken into consideration:—

1. The speed of a plate varies with the quality or character of the illumination. A carefully definable source of illumination must be used which, to a reasonable extent, will have to be comparable in quality to daylight. Probably an acetylene flame standard will be the best for practical purposes, but it must not be screened with coloured glass, as this introduces a variable factor, not capable, or only difficulty capable, of definition. As an alternative, a standard exposure to a light produced by the burning of a given weight of magnesium ribbon at a given distance (say 8 mgms. at 2 mets.) might be used. Magnesium light is a very fair approximation to daylight in quality, and it is not difficult to burn it in such a way that concordant results can be obtained. The amount of ribbon given above burns up in almost exactly two seconds, which might almost be called a very slow snapshot.

2. The speed of a plate varies with the intensity of the illumination. From a sensitometric point of view the product of intensity of illumination into length of time is not equal to exposure (as a constant). In fact, speed increases with increase of intensity into decrease of time, and decreases with decrease of intensity into increase of time.

3. The type of exposure apparatus used will have to be defined. The sector wheel is certainly the most convenient, but I think it is still an open question whether the readings obtained by this method can be considered the best, and whether it would not be better to use a sensitometer of the Spurge type, using a gypsum surface as a reflecting surface. In an apparatus of this form we should be making exposures to varying intensities of light (similar to the exposures which a plate is subjected to in the camera), and not to the same intensity of light for varying lengths of time. In any case, if the

sector wheel is to be used, as being the most convenient, the speed of revolution should be defined, say 10 revolutions per second.

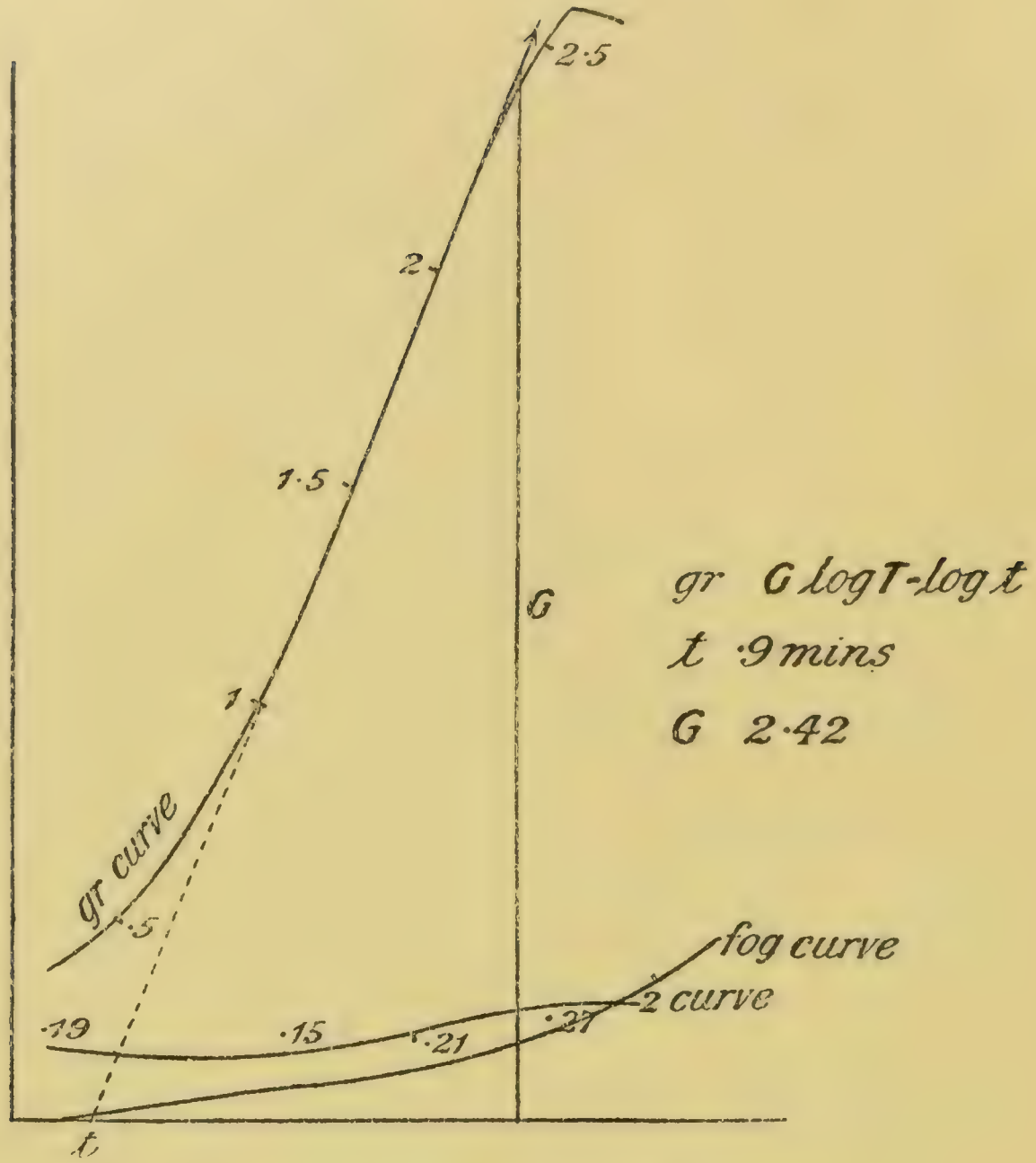
4. Speed readings vary with the strength, temperature and character of the developer, and may even be affected by the quantity of developer used and the size of the developing tray. A good standard developer is the H. and D. pyro-soda developer diluted to half strength. The temperature should be raised to 65°F.=18°C., and the pyrogallol should be added just before development commences. About 100 c.c. per ¼-plate is a good quantity, and a developing tray, at least double the size of plate to be tested, should be used so as to ensure an even flow of developer over the plates. A good fixing bath is an alum hypo bath (5 per cent. potash alum solution, and 20 per cent. hypo solution, mixed in equal quantities). By immersing the plates, without previous washing, in this bath, development can be stopped very rapidly, and by moving the plates all the time, even and clean fixation is ensured. By using the bath fresh, and fixing the plates 15 mins., the colour of the silver deposit in the plates shows a good black, even when pyro-soda is used as a developer.

5. An average fog reading should be taken on the exposure strip close to the low exposures. At this point the fog is not seriously affected by the restrained and weakened developer which is formed in the plate and diffuses out of the gelatine film. This is the case near the higher exposures. The average fog should be deducted from the actual readings and the final readings should not be the result of differential readings.

6. Plates should be backed so as to avoid the influence of halation.

7. Speed varies, at least in many cases, with the development factor, even when no bromide is present in the developer or plate. This is due to mechanical causes, *i.e.*, to the rate of diffusion of the developer into and out of the film and to the weakening and restraining of the developer in the higher exposures. In these the weakened and restrained developer has to be replaced by fresh developer before development can be completed. Development does not start rapidly in the low exposures as it does in the high exposures, but once started reaches its maximum comparatively quickly. For low development factors speed is low, but rapidly rises to a maximum at or about $\gamma = \cdot 8$, then drops slowly but steadily, especially if fog increases much when high development factors are reached. The diagram (fig. II.) shows this clearly, and shows how the γ curve follows a law

Fig 2.



Time of development in minutes logarithmically.

similar to that of the density curve, namely, $\gamma = S(\log. \top - \log. \mathcal{T})$ during the greater part of the useful development factors.

Here γ = development factor,
S = 'rate of development' factor,
$\top$ = time of development,
$\mathcal{T}$ = development inertia.

With a good plate a speed very near the mean speed of the plate is obtained at $\gamma = 1{\cdot}8$ on the H. & D. photometer, and

$\gamma = 2{\cdot}1$ on the Koenig Marten photometer.

Even with good clean plates the difference in speed for different γ's is as much as $\pm$ 30 per cent. from the mean.

e.g. $\gamma = \cdot 8$ $\quad i = \cdot 16$ $\quad$ speed $= 212$
$\gamma = 1 \cdot 8$ $\quad i = \cdot 21$ $\quad$ „ $= 162$
$\gamma = 2 \cdot 4$ $\quad i = \cdot 26$ $\quad$ „ $= 130$

8. The speed of the plate varies with the type of photometer used, and even with the same photometer according to whether more or less diffused light is used or parallel rays are used. With a Koenig Marten photometer the same strips give on an average some 30 per cent. higher γ readings and some 10 per cent. higher speed readings than is the case where a H. and D. photometer is used.

9. The standard apparatus which would have to be used need not I think be very expensive to give reliable results.

In conclusion, I would summarize by saying that to my mind the "standard speed" of a plate will have to be understood to mean "the speed obtained for a standard development factor, when a standard developer has been used at a standard temperature, the plate having been exposed to a standard light at a standard distance for a standard time in a standard type of exposure apparatus, and the readings having been taken with a standard photometer."

Discussion.

Dr. Sheppard said with respect to the conventions which may be adopted, it appears desirable, if the "speed" is to be determined from the characteristic curve, that a common or standardised method of "fitting" the "speed-line" to the points of the curve be decided upon.

Sir W. Abney said he thought that the question of sensitometry ought to be settled by referring it to the different societies of each country. That they should report at a congress and finally settle the standards.

M. L. P. Clerc se félicite de l'appui que vient de donner Sir W. Abney à une communication qu'il compte faire demain, en collaboration avec M. Namias, et au nom de la Commission permanente des congrès internationaux de photographie, pour solliciter les éminents techniciens qui ont participé au congrès actuel de bien vouloir apporter le concours de leurs travaux au prochain Congrès International de Photographie (Bruxelles, 1910).

Prof. Namias: In view of the approaching meeting in 1910 at Brussels of the International Photographic Congress, it appears desirable that the discussion and suggestions concerning the state of sensitometry arrived at be forwarded to this Congress.

On the Eder Solution.

By Dr. Chr. Winther.

The light sensitive mixture of mercuric chloride and ammonium oxalate has been investigated by various chemists. Amongst these Roloff seems to have found that the reaction takes place between the mercuric ions and the oxalate ions. Jodlbauer and Tappeiner have found that oxygen has a retarding influence; Kastle and Beatty, that several substances, amongst which is ferric chloride, have an accelerating influence on the destruction of the Eder solution in light.

I have found that this accelerating influence of the ferric chloride increases with the amount of iron until a certain point is reached. By further addition of ferric chloride the sensitiveness again decreases. In the case of solutions, originally saturated with air, this maximum lies at a mixture of one volume of a 0·0052 molar ferric chloride and two volumes of the Eder solution. This mixture has a sensitiveness about 100 times as great as the iron-free solution. By continual saturation with air the sensitiveness decreases a little, and the maximum goes up to nearly 0·008 molar ferric chloride. With decreasing amount of oxygen in the solution the sensitiveness increases immensely; at the same time the maximum goes towards the smaller concentrations of ferric chloride. After two hours' treatment with a very pure carbon dioxide the maximum lies at 0·00050 molar ferric chloride. This mixture has a sensitiveness about 8,000 times as great as the slowest Eder solution I have had in my possession.

With regard to the catalytic action of the ferric chloride, it was long known that a mixture of ferric chloride and ammonium oxalate on insolation is converted into ferrous salt and carbon dioxide. I have found that dilute solutions of ferrous salts in the dark cause the destruction of the Eder solution into mercurous chloride and carbon dioxide. The catalysis is then caused by the destruction of ferric oxalate in light and the subsequent destruction of the mercuric oxalate by the ferrous salt, which is hereby again oxidised to ferric salt.

The reaction of the ferrous salt on the Eder solution takes a measurable time. On estimation of the amount of mercurous

chloride, which is precipitated for instance after half an hour, a maximum is found at a certain amount of ferrous salt; in the case of solutions saturated with air, this maximum lies at a mixture of one volume of a 0·003 molar ferrous salt and two volumes of the Eder solution. The ferrous salt precipitates much more than the equivalent amount of mercurous chloride, and the proportion between mercurous chloride and ferrous salt increases with decreasing amount of iron; under these circumstances the proportion increases to a value of twenty. After treatment for two hours with carbon dioxide the maximum goes down to 0·000005 molar ferrous salt; under these circumstances the proportion increases to nearly 4000. In this way it is easy to get a test for ferrous salts in a dilution of less than one molecule in a million litres.

I have found that the amounts of iron which give a maximal precipitation of mercurous chloride just correspond with the oxygen present in solution; the more exact examination has shown that it is the oxidation of the ferrous oxalate that causes the destruction of the Eder solution. The less oxygen in the solution, the less ferrous salt is necessary for the precipitation of mercurous chloride. On insolation of the Eder solution containing iron, this limit is reached the sooner, the less oxygen the solution contains, and the greater is consequently the sensitiveness. At the same time the retarding influence of chromic acid and the chromates, as found by Kastle and Beatty, is thereby explained; these substances oxidise the ferrous oxalate very quickly, and thereby prevent the slow oxidation that causes the destruction of the Eder solution.

Further, I have found that an addition of ferric salt retards the precipitation of mercurous chloride by ferrous salt. This retardation is, for small amounts of ferrous salt, quite insignificant, and for constant proportion between ferric and ferrous salt increases with the total amount of iron. On the assumption that the sensitiveness of ferric oxalate in these concentrations is independent of the amounts of iron, then on simultaneous insolation of different mixtures there must be formed equal fractional parts of ferrous salt. The retarding influence of the remaining ferric salt on the precipitation of mercurous chloride is then greater, the more iron there is in the solution. It is then possible that this retardation by a certain iron concentration may be so great that the precipitation of mercurous chloride becomes smaller than in another solution which contains less iron. Both by calculation and by experiment I have found this to be true; the

retardation caused by the remaining ferric salt is able to give rise to a maximum of mercurous chloride at a certain iron concentration.

Experiments made in a current of carbon dioxide have shown that the retarding action of the ferric salt on the precipitation of mercurous chloride increases rapidly with decreasing amount of oxygen in the solution. With smaller amounts of oxygen this retarding influence must therefore be detected at smaller amounts of iron, and the iron maximum has to be displaced in the same manner.

The fact that both the retardation by oxygen and by chromic acid is found in the pure Eder solution suggests that this pure solution also contains a little iron. Desiring to see the importance of this impurity, I have investigated different commercial preparations, namely, four from Kahlbaum and six from Merck. The purest mercuric chloride from Kahlbaum was mixed with the purest ammonium oxalate of the same origin, and similarly in the other cases. The five portions of Eder solution thus made were insolated at the same time:—

Kahlbaum	I.	4·04
	II.	2·10
Merck	I.	2·77
	II.	2·26
	III.	1·47

These experiments show that in its usual form the Eder solution has not to be used for comparative investigations. This fault can be corrected by addition of a suitable amount of ferric chloride. At the same time the influence of oxygen can be brought down to a minimum.

The less iron in the Eder solution, the smaller is the sensitiveness. Also the retarding influence of the oxygen increases with the amount of iron up to a certain point. These and other similar facts go to show that the pure, iron-free Eder solution is practically insensitive on insolation.

Jodlbauer and Tappeiner have found that some fluorescent dyes accelerate the destruction of the Eder solution. My observations give the following results with eosine:—

	Pure.	With Eosine.
Red	0·47	0·85
Green	0·47	3·74
Blue	2·33	4·25

It is consequently a real optical sensitisation.

According to Eder the mercuric oxalate absorbs much more of the active rays than either mercuric chloride or ammonium oxalate. In order to test this I have put in the inner glasses a very sensitive mixture of ferric chloride and Eder solution, and round about this either mercuric chloride, ammonium oxalate, or a very pure Eder solution. After insolation in one hour the Eder solution in the outer vessel was still quite clear. In the inner glasses there were precipitated in all cases equal amounts of mercurous chloride. An optical extinction is consequently not to be found in the Eder solution.

The Present Condition of Etching.

By A. J. Newton, *London.*

Etching has not hitherto obtained much attention from investigators, but at the present moment there is great activity in the introduction of mechanical aids to etching, and this will probably arouse a good deal of further inquiry.

The word "etching" is derived from the Dutch word "Etsen"—to bite, and although it may be justifiable to consider as etchings plates bitten out by electrical means, I propose to limit my remarks to those etchings which are bitten out by acids or similar mordants, since these are the current methods.

The process of etching therefore consists in transferring by some means—generally photo-mechanical—a design on to the surface to be etched. In the case of relief line etchings the design is made of acid-resistant material, and the remainder of the metal left bare; in the case of intaglio line work the acid resist covers that part of the metal which represents the white ground. Engravings known as half-tone etchings are in effect line etchings. Those intaglio etchings known as photogravures are somewhat different, as the tones are produced by the respective depth of biting out, resulting in different thickness of printing ink being printed from the various tones. In the first cases the metal is either completely bare or completely protected; in the last case the metal is only protected in degree by a varying thickness of resist, which in its thickest part will ultimately allow a mordant to penetrate.

"Etching" properly so called is an artist's intaglio process, and we are therefore not concerned with it, except as tracing its history towards the photo-mechanical methods with which we are to deal.

Mr. Hind, in his recently published "Short History of Engraving and Etching," says:

> "The process of etching, in its widest signification, was practised by the goldsmith, metal-chaser, and more particularly by the armourer and gunmaker, long before it was used for the production of prints. It is perhaps impossible to date any weapon with etched decoration before the last three decades of the fifteenth century, but instructions for etching on iron are found in a MS. of the earlier part of the

century, and there is every reason to suspect that the method was known well before the fifteenth century, if not in antiquity.

"The practice of taking impressions on paper from etched plates may possibly go back to the last few years of the fifteenth century, but no date can be assigned to any etching earlier than 1513, the year given on Urs Graf's "Girl Bathing Her Feet," of which the only impression known is in Basle. Then there are some five etchings by Durer, dating between 1515 and 1518. The Gethsemane and the Canon are most powerful works, but Durer was probably ill content with the coarseness of the lines attainable on iron, which remained for a considerable time the common material for etching in Germany. The use of iron may have been determined rather by the conventions of an art which was chiefly applied in the armourer's workshop than from any lack of knowledge of a suitable mordant for copper."

In original etching as now practised the artist scratches his design through an acid resist and allows the acid to act on the bare metal. When he thinks certain of the lines are sufficiently etched he stops the etching by painting over them acid-resisting varnish, and goes on etching further for those lines which are not sufficiently etched. The same discriminating handwork is applied to the improvement of photo-mechanically etched blocks, and is known as fine etching.

In addition to iron and copper, pewter, stone, and even wood have been used for etching. At the present, practically only two metals are used—namely, copper and zinc, though some brass is used, and occasionally steel.

Dr. Eder states in his "Handbuch" that A. Dembour painted in acid-resisting ink on copper, and etched in relief for printing. He published a book in 1835 with eight illustrations, which may probably be the first relief etchings, while Mr. Bolas says:

"Zinc as a basis was used by Senefelder either towards the end of the last century or at the beginning of this century, and although I am not aware of any definite evidence that he etched his zinc into high relief as he did his earlier stones, his work bore fruit later, and in 1822 Eberhardt published a little book giving instructions for etching brass and zinc into relief. Husnik attributes to Eberhardt priority in the

matter of the application of relief zinc etching to typographic printing, but the process was very little used until Gillot, of Paris, about forty years later put it on a commercial basis."

Eder, however, thinks that Blasius Hofer, in Vienna, may have been the first, in 1840, to produce zinc etchings in relief. In 1850 Gillot introduced "Paniconography," but it has been named after him "Gillotage." He wrote, printed, or transferred an impression on the usual lithographic transfer paper, and then put this down on the prepared zinc plate, where the image was strengthened by rolling up with ink, and further strengthened by dusting with a resinous powder. This plate being now warmed, to promote adhesion of the image and the incorporation of the resin, the first etching is performed with weak nitric acid, after which the plate is again inked, dusted with resinous powder, and heated, this time sufficiently to make the mixture of resin and ink run down the nearly vertical sides of the relief, and thus protect the lines from undercutting. After a number (five to ten) of operations like this, the plate is cleaned, the face is protected with a rolled-on ground, and a final etching serves to remove any sharp edges of the steps formed by successive etchings.

In the 'fifties the first indirect application of photography to relief etching was made by Charles Negre. He made a reticulated gelatine relief, inked this and transferred to zinc, and then etched by Gillot's method.

Gillot's son, Charles Gillot, was the first to use photography direct, in 1872, by covering the zinc plate with a sensitive solution and exposing under a negative.

We need not go into the further history of zinc etching, which has consisted in the improvements in the use of bitumen and the substitution of the bichromated colloid resists (as albumen and fish-glue), and of the introduction of the enamel process, of the Viennese method (as against the French) of etching, and the American method of powdering four ways.

With regard to the metals used, I will not go into the sources or nature of zinc, except to state that little appears to have been done to determine the particular impurities, without which zinc would not etch at all, that are most desirable in the zinc, and the right proportions of such impurities.

Novak has recently published in the "Photographische Correspondenz" some analyses of various commercial samples, all of

which samples he found suitable when they had not to be heated first. But the hot enamel process of making typographic blocks entails the heating of the insoluble fish-glue until it has become carbonised, and in doing this the zinc becomes crystalline and very fragile, and renders it more or less unsuitable for the subsequent operations of etching and printing.

The following are the results of two of these analyses of Novak's:

	No. 1.	No. 2.
Lead	1.6 %	... 1.23 %
Cadmium	0.209 %	... 0.072 %
Iron	1.0298 %	... 0.0117 %
Arsenic	Trace %	... Trace %

Sample No. 1 seemed suitable for all kinds of work, but No. 2 did not give good results with the hot enamel process. Thus zinc with a greater percentage of cadmium is preferable for the hot process, and lead is not so detrimental to quality of plate as many have asserted.

A good deal of trouble is often caused by the want of adhesion of the enamel film in the etching bath. This is presumed to be due to the crystallization of the zinc caused by heating. Investigation is required as to the cause of this—as to whether it varies with the same resist on different samples of zinc. Tschorner ("Photographische Correspondenz") has investigated the matter with regard to various qualities of resist, and concludes that certain resists, and resists hardened or tanned after exposure, withstand the acid better than others.

Steel, which is sometimes used for etching, shows just the same difficulty with regard to keeping the enamel on. Perhaps the cause here is the greater difficulty in getting the steel thoroughly clean. Steel is extremely hard and durable, but it is very inconvenient to keep from corroding rust, and so it is only used for work on die presses.

Brass can be used for etching purposes exactly like copper in very nearly all respects, although it does not retain the enamel quite so well; still, this difficulty can now be overcome, and from the printer's point of view brass is superior to either of the other two metals in that it would not corrode like either copper or zinc, but it is very little used in England, apparently because the price is practically the same as for copper, to which engravers and printers have become accustomed.

Copper is the chief metal now used in engraving half-tones, though it is possible that the introduction of the etching machines, together with the keen competition in the sale of etchings, may lead to a considerably greater use of zinc, on account of its lesser cost.

The advantages of copper are its high melting point (1100° C.), its durability, its practical freedom from corrosion in air, and, above all, the fact that it retains the enamel film well and etches easily.

With regard to the mordants used, it is not worth while to mention the numerous different ones that have been proposed, as there are really only two in general use at the present time—namely, nitric acid for zinc and perchloride of iron for copper.

In etching with zinc the temperature is very much raised, but a peculiarity of the Mark-Smith etching machine is to keep the temperature lower—due probably to the influence of cold air drawn into the machine.

The etching mordant for copper is iron perchloride. Of course, many acids will etch copper, but perchloride has become universal because it etches fairly quickly, evenly, and without giving off any fumes.

The temperature of the solution should be carefully regulated, because it is a thick solution. The colder it is the more viscous, and this has an important effect on its rate of action. Some experiments I made some time ago showed that the solution of 110° Fahr. etched in two-fifths the time the solution took at 60°—*i.e.*, two as against five minutes.

With regard to the actual method of etching, it may be performed in several ways. First, one can have a small dish not much larger than the plate required; place the plate in face upwards, and commence to etch. This is a quite unsatisfactory method, since the products of the etching remain on the metal at the point of etching—gas bubbles in the case of zinc, and copper chlorides in the case of copper.

The obvious way to overcome this trouble is to brush lightly the surface of the metal all the time, and this is the method practised frequently. It has the disadvantage of causing the side spread of the acid action to be greater than is necessary, and the result is that the high lights are etched to a point before there is any appreciable depth obtained. That is why, where this method is adopted, it is often necessary to roll up and give a deep etching in order to get a good printing depth. Another remedy is to turn the plate upside-

down and etch film downwards. But this will not answer in the case of zinc, because the bubbles still collect on the surface of the zinc and impede the etching exactly as before; but in the case of copper it is no doubt very advantageous, as the products of the reaction, being heavier than the solution, fall to the bottom of the dish, and allow fresh acid to always have access to the bare metal that is required to be dissolved. Another method is to use a large bath and to violently rock the solution. This removes the reaction products. At the same time, it is to some extent subject to the same disadvantage as brushing—namely, it etches the lighter tones quicker than the darker; that is, the sideways action is somewhat more vigorous. But a large bath has the advantage of keeping the solution cool.

A question of importance is, at what strength iron perchloride does the etching have its greatest depth in a given time, and how soon is such a solution exhausted. If we know these two things we may be able to arrive at the most economical way to use the mordant, and the way to do the work with the greatest amount of regularity and precision.

I have had careful experiments made showing the exact weight of copper dissolved in a given time by varying strengths of perchloride of iron of a given quantity. From the slide shown you will see that iron 35° Beaumé is on the whole the quickest solution, and this is confirmed by practical tests and further measurements of a graded strip negative and prints made from the etching from it.

All the inventors of etching machines claim that speed of etching is increased, and to do this they must conform to the conditions of removing the reaction products from the etched spaces, and bring fresh acid to bear on them. The more force with which this is done, apparently, the better.

The first application of machinery to etching is probably the power-rocked tub, and I have here an illustration published in 1895 of the bath attachment used in the firm of Carl Hentschel, and also a slide showing the latest pattern catalogued of the same device.

A little later on we have an actual illustration of a simple contrivance to effect this—namely, in "Anthony's Bulletin," June, 1896.

The Levy acid blast etching machine was the first commercial machine to be described, and I believe the first on the market. It was first used in the office of the "Boston Herald" in the spring of

1900. Levy's first patent is No. 2710, 1899; date of application, 7th February, 1899; accepted, 18th March, 1899. In this he claims, among other things, the process of etching metal plates which consists in projecting or spraying a mordant upwards against a plate supported horizontally in a chamber or etching box, but chiefly the process of etching metal plates which consists in atomising or spraying a mordant by means of compressed air against the face of a plate having thereon the design through a resist so that the dynamic force of the impact will accelerate the chemical action of the mordant for the purposes set forth.

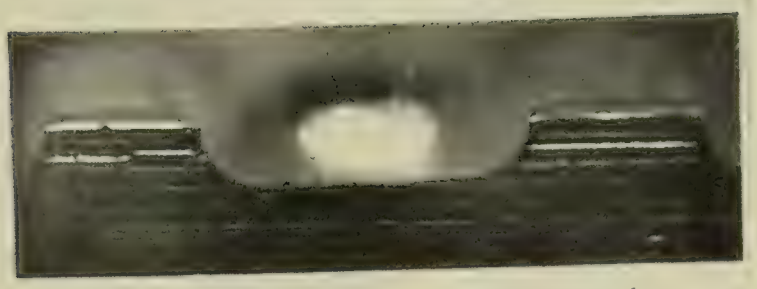
And the heat evolved by the erosive action of the mordant will be absorbed by the expansion of the air.

In patent No. 18869, 1906, applied for 23rd August, 1906, and accepted 3rd January, 1907, this last claim is not mentioned, but the chief claim is means for drawing from the etching chamber the vapours, fumes, and gases generated therein during the process of etching, and means for condensing the vapours and returning them in liquid form to the etching chamber, and means for simultaneously producing in the etching chamber a partial vacuum and in the air chamber pressure in excess of the pressure of the atmosphere.

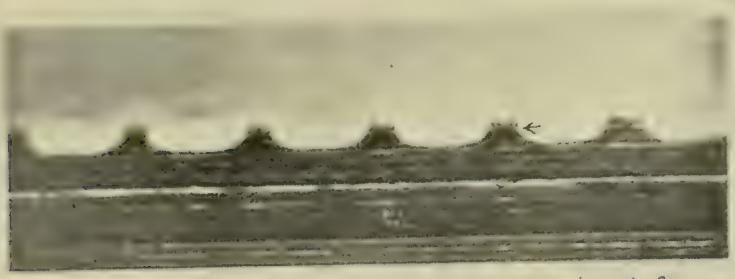
One point exclusive to the Levy machine is the opportunity of varying pressure as well as time and acid.

The next machine I believe to be Holstrom's, which I saw at work in Germany in 1904. Holstrom's patent is No. 4317, 1903 He claims an etching apparatus provided with a receptacle to contain the etching fluid and means for supporting the metal plate or the object to be etched, characterised by one or more rotary winged wheels, or rotary perforated cylinders or other similar rotary spreaders mounted in the said receptacle and partly immersed in the fluid, which spreaders take up fluid and throw it against the plate or object to be etched, and the said plate or the like being, if desired, mounted in an inclined position substantially as described.

Thorpe's patent is No. 12507, of 1904; date claimed, 4th June, 1903; applied for in U.K., 2nd June, 1904; accepted, 22nd December, 1904. This machine is one in which the acid is pumped from a mill below and then rains down on the plate from above. The principle is the same as the Danesi machine. Danesi has obtained a patent for his machine in France, published 12th August, 1908; applied for 16th March, but it was described at a congress in October, 1906, in Milan.

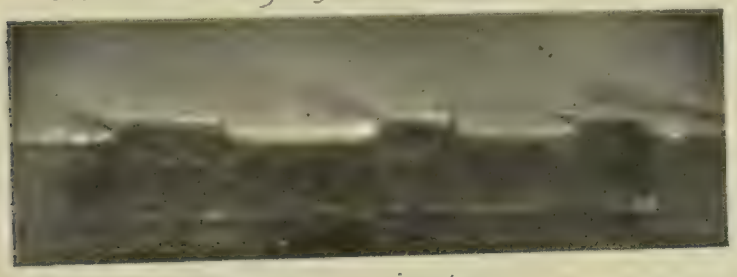


Coarse Half Tone Levy Machine

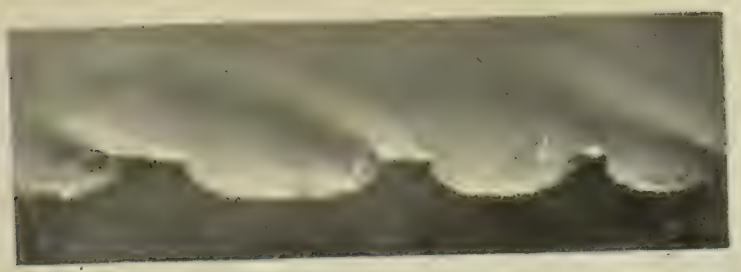


Half Tone Etching with enamel resist left on showing apparent undercut Levy Machine

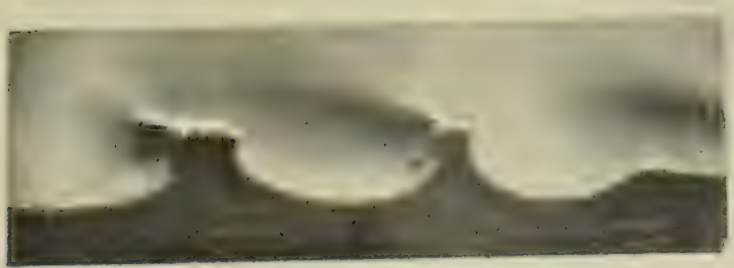
Line Etching by Levy Machine.



After 1 minute.

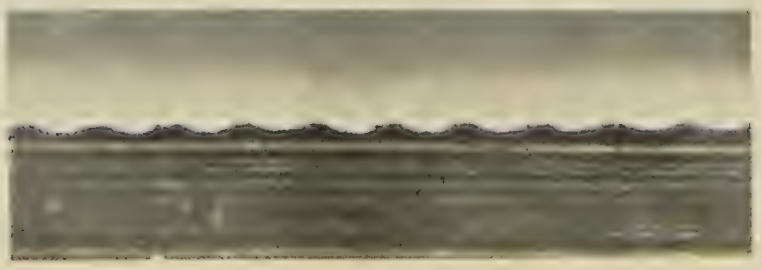


After 2 minutes

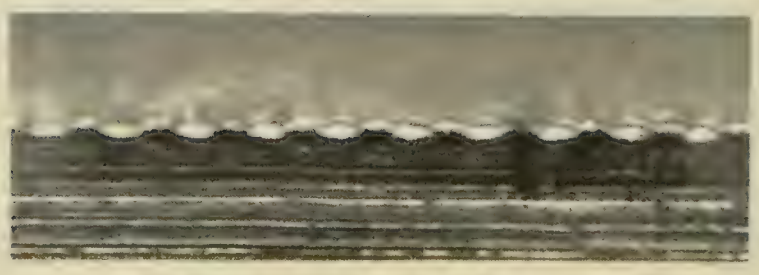


After 4 minutes

Magnified 28 times



Albert Machine



2 min

Levy Machine

Levy Machine

14 min

The Mark Smith patent is No. 25744, 1904; applied for 26th November, 1904; accepted 6th July, 1905.

Claims the process of etching a plate for printing which consists in treating the under and prepared side of such a plate with an acid or like spray produced and thrown against the underside of the plate by means of a brush or roller rotating in the acid.

The Albert etching machine is Patent No. 23392, 1906; date claimed, 7th November, 1905; applied for the U.K., 22nd October, 1906; accepted, 16th May, 1907; and claims in processes for etching plates and the like by means of a liquid, the method of producing a continuous succession of small movements of the liquid in contact with the surfaces of the plate, as and for the purposes set forth.

The use in combination with an etching trough of an agitating device having a series of comb-like ridges or prongs arranged and operating as described.

Barthomew and Bussy, patent No. 20321 of 1906, was applied for 12th September, 1906, accepted 6th December, 1906, and claims "in etching half-tone, line, and other process printing plates means whereby the surface of the plate to be etched, whilst in a horizontal, or approximately horizontal position, is brought into rapid and repeated contact with the surface of the acid bath by imparting a vertical reciprocating motion to the plate or to the bath, or to both, for the purposes specified."

The Concewitz is a machine that holds the plate on a disc which, on being lowered into the solution is capable of being whirled, and is the opposite of Dr. Albert's idea, inasmuch as the plate is moved while the solution remains stationary.

The Holt machine is constructed of the usual tub, with a disc that revolves in the liquor. This disc is provided with blades constructed in such a manner as to provide the constant agitation in little whirlpools of the acid. The Holt machine is therefore a sort of combination of the Concewitz and Albert principles.

It is as well not to end this catalogue of machines without mentioning the "Aerograph" of Mr. Amstutz, which is not an etching machine at all, but may ultimately do a great deal to entirely replace the process of etching for engravings.

I have made some experiments to show the action of the acid on the metal, and, firstly, I will show comparative slides of the same tone etched on as many different machines as I have been able to get used at present. From this you will see the superiority of the machine over hand etching, and I think you can draw your own conclusions as to which machine gives the best result so far.

Discussion.

M. L. P. Clerc fait remarquer que l'*efficacité* d'un procédé de morsure ou d'une machine pour la morsure pourrait être définie comme étant le rapport $\frac{AO}{OB}$ des deux axes de l'ellipse qui limitent l'affouillement dû au mordant, ce rapport étant égal à 1 lorsque la vitesse *latérale* et la vitesse *normale* de la morsure sont égales; par exemple, dans le cas de la morsure face en dessous d'une planche de cuivre dans une solution de perchlorure de fer. Ce sont des recherches de cet ordre, commencées avec M. Calmels, qu'il se proposait de communiquer au Congrès, mais qui n'ont pû être suffisamment avancées, et qu'il verra très volontiers entreprendre par d'autres chercheurs.

Abstract of the Report on Acid Resists.

By W. Gamble.

Since the advent of photographic processes of etching very different conditions have been created to those which existed before, when waxes, resins and asphaltum formed the leading ingredients of acid-resisting compounds.

It has been found that talc, silica, sulphur, graphite, carbon and other inert bodies can be made use of as acid resists under suitable conditions.

Also one metal can be made use of as a resist, by choosing such an acid that will not attack it, though the base plate on which the metal resist is laid will not be attacked.

Colloid bodies can be made to form acid resists by making them light sensitive by means of bichromates—fish glue being the most generally used. Its sensitiveness can be increased as shown by Ricard and Clerc by adding erythrosine or other dyes, though Tschörner had endeavoured to show that such additions had no practical value. This was contrary to the experience of practical workers here in London.

It has been found by analysis of Kayser that bitumen was most sensitive when it contained the largest proportion of sulphur,

Syrian and Trinidad bitumens containing about 10 per cent. Valenta had endeavoured to increase the light sensitiveness of bitumen by introducing sulphur dissolved in pseudo-cumene, but the process had not become commercially practicable.

The general result of any increase in sensitiveness of photographic films was an improvement in their quality as acid resists.

Dragon's blood was a very valuable product for making acid resisting images, but was very variable in its composition, often containing as much as 40 per cent. of earthy matter. It had been found possible to eliminate this by purification, but it was not yet possible to determine whether this was of sufficient advantage.

Some formulæ for the fish glue enamel contained alkaline citrates originally suggested by Professor Namias, with a view of increasing their sensitiveness. Generally citrate of iron and ammonia were used.

Hardening baths for fish glue films had been used in the so-called "cold enamel" processes.

Seyewitz had published valuable information on the hardening of colloid bodies with chromium compounds.

Substratum films had been applied under the fish glue coating to improve the acid-resisting qualities of the image.

The use of a soluble film of gelatine etched through with perchloride of iron is also referred to—as used in the heliogravure process—the resist depending on the fact that the strongest solution of perchloride of iron goes through the film most slowly.

Discussion.

M. L. P. Clerc fait remarquer que les citrates alcalins ont été proposés par M. Namias, non pour accroître la sensibilité mais pour accroître la durée de conservation ; il a constaté en effet une très grande efficacité au citrate d'ammoniaque tant pour la conservation des couches sèches que pour celle des solutions de colle bichrômatée destinées au procédé émail, mais il n'a pu reconnaître à ce corps aucun effet utile sur la sensibilité.

Prof. Dr. Namias dit : Je confirme ce qu'a dit M. Clerc, c'est-à-dire que l'addition à la "fish-glue" et à l'albumine de citrates alcalins que j'ai conseillé il y a plusieurs années a surtout le but d'augmenter la stabilité de la couche et de faciliter le dépouillement.

Au lieu d'augmenter la sensibilité de la couche cette addition diminue un peu la sensibilité.

L'addition de citrate de fer ammoniacal, dont parle M. Gamble, peut augmenter la sensibilité, car ce composé prend part un peu à la réaction qui se produit à la lumière en hâtant la réduction du bichrômate en conséquence de la réduction que le sel de fer lui-même subit.

Major-General J. Waterhouse said : With reference to the increase of sensitiveness in films of asphaltum by the addition of erythrosin, he thought it was probably caused by the evolution of the halogen, because he had found that iodine and chlorine had a very strong effect in rendering asphaltum insoluble. Erythrosin alone showed also a strong oxidising effect on gelatine under the influence of light, the exposed parts being rendered more or less insoluble, as with bichromate. He had also tried increasing the sensitiveness by the addition to the sensitising solution of thiophene, which contains a quantity of sulphur ; but he could not now remember whether any distinct sensitizing effect was observable. He had also found long ago that the addition of citric acid to the solution of gelatine and bichromate of potash used for coating photo-lithographic paper, enabled it to be kept longer in good condition in the damp hot climate of Calcutta.

M. A. Seyewetz fait observer, à propos des substances qui insolubilisent la gélatine, qu'il a indiqué l'emploi de la quinone. Ce produit, qu'il a fait breveter pour le tannage des peaux, donne avec la gélatine une insolubilisation supérieure à celle que donne le chrôme en ce qui concerne la résistance du produit insolubilisé à l'action des acides et des alcalis. Il est possible que ce produit puisse rendre des services dans l'ordre des applications signalées par M. Gamble.

Abstract of the Report on Colloid Chemistry in Relation to Photography.

By S. E. Sheppard, D.Sc.

Colloid chemistry, the science of the border region of the microscopic and amicroscopic.

Nature of colloid systems : classification of colloids.

(*a*) Colloid solutions, hydrosols, their preparation and nature. Sols in the photographic process (colloidal silver salts).

(*b*) Reversible and irreversible phenomena.

(1) Irreversible coagulation.

(2) Reversible coagulation, return by pectisation. Illustrated in the "ripening" of emulsions.

(3) Gelation reversible and irreversible phenomena in setting and swelling. Influence of salt solutions. Illustrated in photogravure etching, and in all processes in gelatine films. The theory of tanning and hardening.

(*c*) Adsorption; the interactions of colloids and crystalloids; interaction between colloids. Non-applicability of stoichiometrical laws. Proportions and properties, functions of the original-reaction conditions. Illustrated by emulsion-making phenomena. Colloidal phenomena in

(1) Latent images and printed images.

(2) The developed image.

(3) Adsorption in fixation.

(4) Adsorption phenomena in processes of reduction and intensification.

(5) Adsorption in toning processes. Some general conclusions and bibliographical notes.

Discussion.

Mr. F. F. Renwick asked: Are not the phenomena which Dr. Sheppard has classed under the name "hysteresis" of gelatine and other colloid solutions more simply explicable on the assumption of very sluggish changes in the degree of molecular complexity of the material in solution.

On the question of the nature of the latent image, it has always been difficult for the speaker to accept a definite chemical breakdown as being brought about by the action of light on the ground of energy considerations, the quantity of light energy needed to produce a latent image in the fastest plates being so exceedingly small, and he has therefore inclined to the view that a breakdown of a delicate unstable molecular complex to a simpler developable form offered a more intelligible explanation.

The Use of Agar-Agar in Photography.

By W. F. Cooper, B.A. (Cantab), F.C.S., W. H. Nuttall, F.I.C., F.C.S., and G. A. Freak, B.Sc., A.I.C.

Agar-agar, a gelatinous product derived from certain sea-weeds, has been familiar to bacteriologists as a culture medium for many years, and those unique and peculiar properties which led to its introduction into bacteriological technique, also, to a certain extent, suggested to the photographic chemist that it might prove a valuable substitute for gelatine in the preparation of photographic plates and papers.

As far back as 1882, Mitchell proposed to substitute agar for gelatine in the preparation of photographic materials for use in tropical countries, and in due course, several patents were obtained for this purpose. Manipulative difficulties and inconsistent results have, however, prevented photographic manufacturers from placing agar products on the market to any great extent, and, at the present time, the manufacture of agar papers is confined to a few firms in England and Germany, while, so far as the authors are aware, agar plates have not proceeded beyond the experimental stage.

Agar is obtained from certain sea-weeds found on the coasts of China and Ceylon (Gelideum corneum, Fucus spinosus, and Fucus amylaceus), and the commercial article usually appears in the form of long fibrous translucent strips. Its principal constituent, to which it owes its gelatinising properties, is gelose, a substance which appears to be allied to the gums, inasmuch as it yields galactose and other sugars on hydrolysis, and mucic acid on oxidation.

When soaked in water, agar swells considerably, but complete solution is only effected at a temperature approaching that of boiling water. In actual practice, the agar is allowed to soak in running water for twelve hours, and is then dissolved by heating in a boiling water bath for thirty to forty minutes. Filtration is always necessary and is usually effected by squeezing through fine muslin, and then filtering repeatedly through Chardin filter paper by means of a steam pressure funnel. The filtrate is quite clear, and of a slightly yellowish tinge. On cooling to a temperature of about 32–35°C., according to the concentration, it suddenly solidifies to an opalescent jelly from which, on standing, a certain quantity of

water is expressed. An agar jelly can only be remelted at a temperature of about 90–100°C., a fact of considerable importance from a photographic point of view.

The gelatinising power of agar is exceptionally great, roughly about eight times that of gelatine. Allen states that a 0.2 per cent. solution is capable of setting.

The more important advantages of agar may be summarised as follows:—

(1.) Thinness of pellicle. Since the gelatinising power of agar is eight times that of gelatine, it follows that the dried pellicle is proportionately thinner, although it may contain the same quantity of silver halide as a gelatine film. For present purposes it is unnecessary to dwell upon the advantages of a thin pellicle; suffice it to say that a lantern plate, prepared with an agar emulsion, was intensified three times with mercury and silver in five minutes, and yet showed no stains due to insufficient intermediate washing.

(2.) High melting point of agar jelly. It has already been pointed out that in order to redissolve an agar jelly, the temperature must be raised almost to that of boiling water. Hence, in the treatment of plates and papers prepared with agar, hot solutions may be used and much saving of time in washing may be effected by the use of hot water. Further, it is possible to rapidly dry the washed prints and plates before a fire without fear of "running." For a similar reason, agar lantern slides are not so liable to injury by the heat of the projecting lantern.

The high melting point also enables the photographic manufacturer to dry the coated paper at a temperature impossible with gelatine films. The authors have shown that it is possible to coat, dry and roll the paper in a continuous operation. This was accomplished by passing the coated paper through a narrow box 55 feet in length, through which a current of hot air was pumped. The temperature of the air current varied from 84°C., at its entrance, to 43°C., at its exit. The paper travelled through at a speed of four feet per minute, and at its exit was found to be completely dry.

(3.) Inertness of agar towards photographic salts. From a photographic point of view, agar possesses a distinct advantage, inasmuch as it is unaffected by many reagents which precipitate gelatine. It is therefore possible to incorporate in an agar emulsion, toning salts which are inadmissible with gelatine—as for example, salts of platinum.

Agar is readily decomposed by warming with free acids or alkalies, and then loses its gelatinising power. The products of hydrolysis of agar are sugars; those of gelatine are leucine and allied amino-acids. It would appear that this difference may have an important bearing on the relative limits of maturing of emulsions in agar and gelatine, for it is conceivable that the products of hydrolysis of gelatine, being substituted ammonias, would be more liable to fog an emulsion during ripening, than would the sugars produced from agar. Not being practical emulsion makers, however, the authors have been unable to verify this theory.

(4) Agar has always appealed to the manufacturer on account of the many rich tones which it gives with self-toning printing out papers, *i.e.*, papers coated with emulsions containing gold, and capable of simultaneous fixation and toning by simple immersion in hypo. With agar papers the tones so obtained are distinctly different from those given by gelatine under similar conditions, the tones of the former being rich browns.

In seeking for an explanation of this difference in tones, it was decided to compare their halogen-absorbing powers, although the authors were aware that it is customary to regard the sensitising action of gelatine as being more largely due to a physical effect, than to its absorbing action on halogens, though doubtless this does play some part.

The iodine-absorbing powers of agar and of five different samples of gelatine were determined at four different temperatures, and after three different periods of time. In order to prevent loss of iodine by volatilisation, the estimations were carried out in a closed titration flask, in the cork of which were fitted two burettes, for the iodine and thiosulphate solutions respectively, and a right-angled tube fitted with thick rubber tubing and a screw clamp. The flask, containing the agar or gelatine solution, was closed, and placed in a water bath, maintained at the requisite temperature by means of a thermo-regulator. Partial exhaustion of the air was then effected through the right-angled tube, the requisite quantity of iodine solution run in, allowed to act for the necessary time, and then titrated with thiosulphate, the end point being indicated by starch solution introduced by suction through the right-angled tube. The results are shown graphically in two series of curves.

Fig. 7 is a graphic representation of the relation between iodine absorption and temperature during a constant time—five minutes,

from which it is obvious that gelatine has a considerably greater capacity for iodine absorption than has agar. This is more strikingly shown in Fig. 9, in which case the iodine was allowed to act for sixty minutes. At 50°C., for example, agar has absorbed barely 2·5 per cent. of iodine, while, in the case of Nelson's gelatine, the amount absorbed is about 6·75 per cent.

Fig. 6 represents the relation between iodine absorbed and time at constant temperatures for agar. It is only when the higher temperatures are reached that the iodine absorption increases with the time ; thus, at 35°C., the lowest temperature available with agar solutions, the curve is almost horizontal. For purposes of comparison, similar curves for Heinrich's gelatine are shown in Fig. 3. In this case the increased absorption of iodine with the time is more obvious. The results of the estimations of four other samples of gelatine are represented by the curves on Figs. 1, 2, 4 and 5, but as there is little variation, it is unnecessary to discuss them.

The lower halogen-absorbing power of agar, taken into consideration with the relative thinness of the agar film on the plate, shows that the halogen-absorbing power of an agar film per unit area is only about 5 per cent. that of a gelatine film. The fact that this does not appear to have any marked effect on the sensitiveness of an agar emulsion tends to show that the physical properties of the sensitising medium play a much more important part than do its chemical ones.

When a solution of iodine in potassium iodide is added to a solution of agar, a very characteristic purple-red colour is produced. On heating to 27-30° C. (according to the relative quantities of reagents), this colour turns to yellow, but returns on cooling, a change which may be repeatedly effected. This coloration appears to be analogous to the starch and iodine reaction with this difference, that in the case of agar the production of the colour is dependent on the presence of an iodide; the purple colour reaction fails with an alcoholic solution of iodine, a greenish-yellow colour being the result.

Agar in solution is comparatively stable, and in the absence of free alkali or acid, may be boiled for several hours with impunity. In the presence of free alkalies or acids, however, rapid hydrolysis results, and the decrease in viscosity of the solution forms a convenient measure of such change. Ignorance of this fact was the cause of many failures in the earlier work with agar emulsions. As

might be expected, caustic alkalies and mineral acids have the most rapid de-gelatinising action; in the case of salts and of organic acids the action is considerably less. The action of some of these reagents at 50°C. has been roughly determined by the authors, and their results are shown graphically in Fig. 10. These results are sufficiently accurate to give some indication of those acids, which are to be avoided in the preparation of agar emulsions. Thus, for example, tartaric acid, a common constituent of gelatine emulsions, is inadmissible with agar.

In conclusion, it must be admitted that the subject is open to much further investigation, and the authors' observations lead them to believe that it is on physical lines, rather than chemical, that further inquiry should be prosecuted.

Preliminary investigations on the relative powers of agar and gelatine in restraining the reduction of silver halide by a developer have promised interesting results.

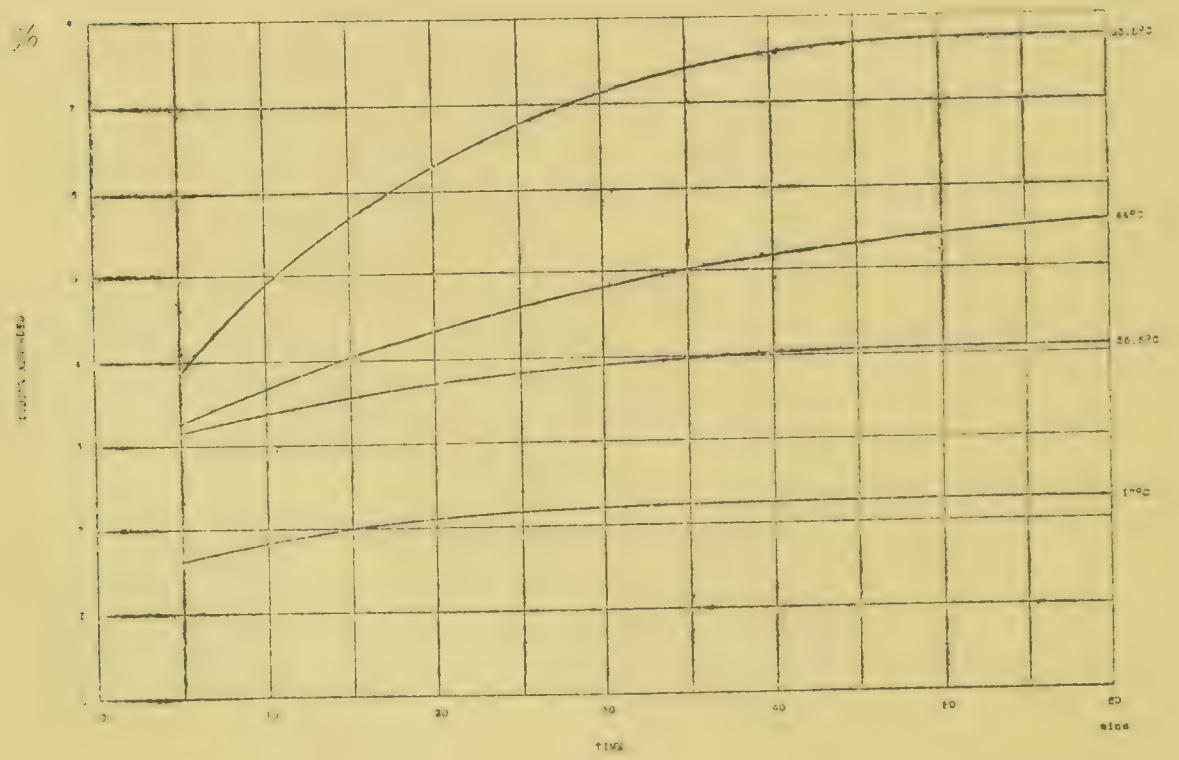


Fig. 1.

Iodine Absorption of Nelson's No. 1 Photo-gelatine.

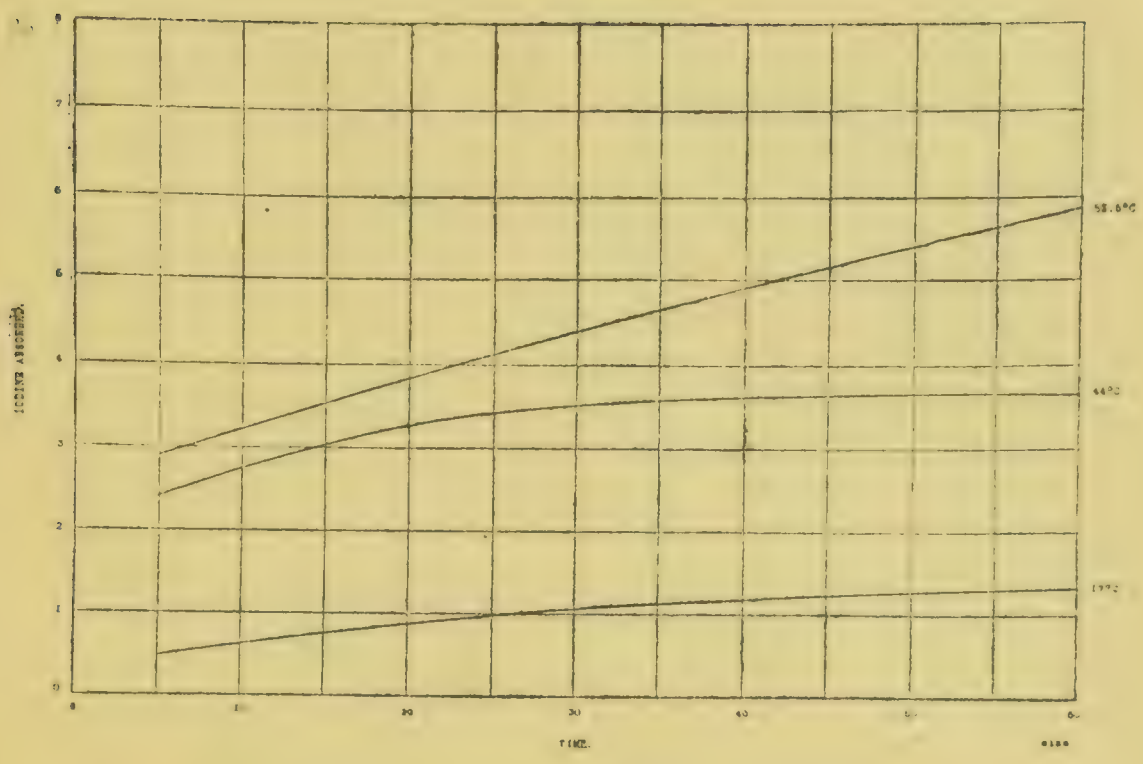


Fig. 2.

Iodine Absorption of Coignet's Gold Label Gelatine.

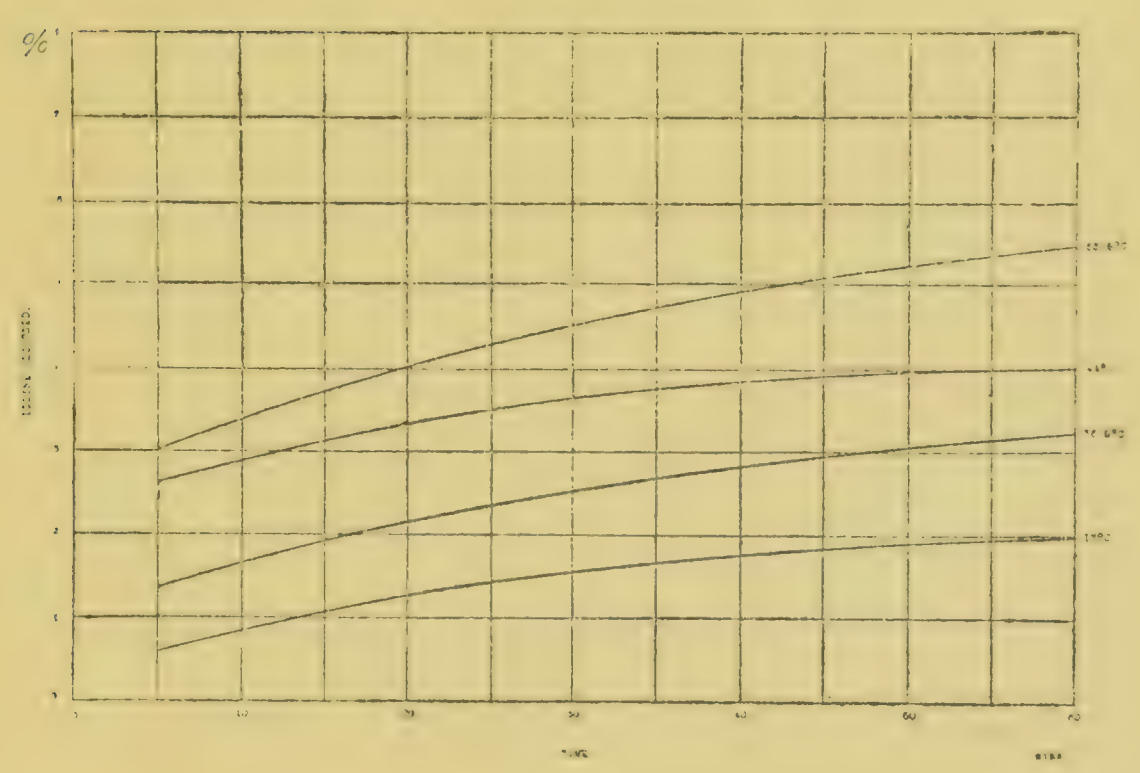


Fig. 3.

Iodine Absorption of Heinrich's Gelatine.

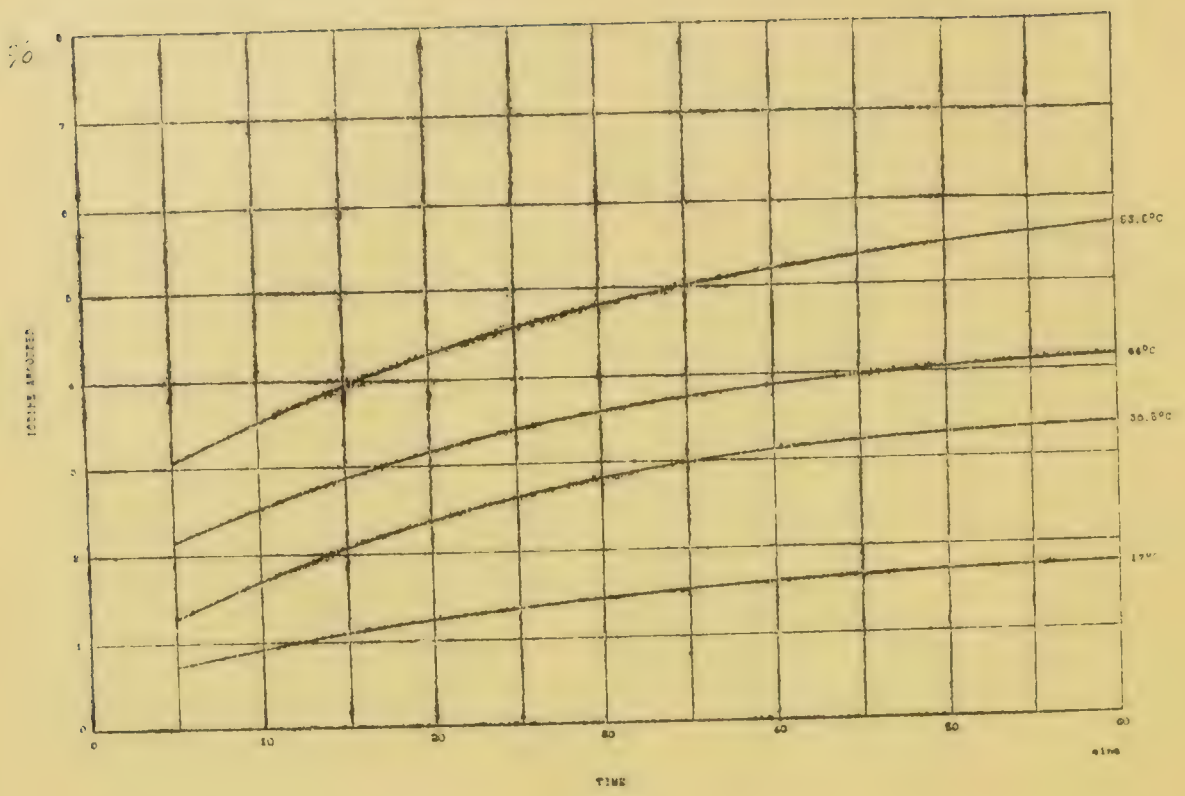


FIG. 4.

Iodine Absorption of Gelatine A. (Soft).

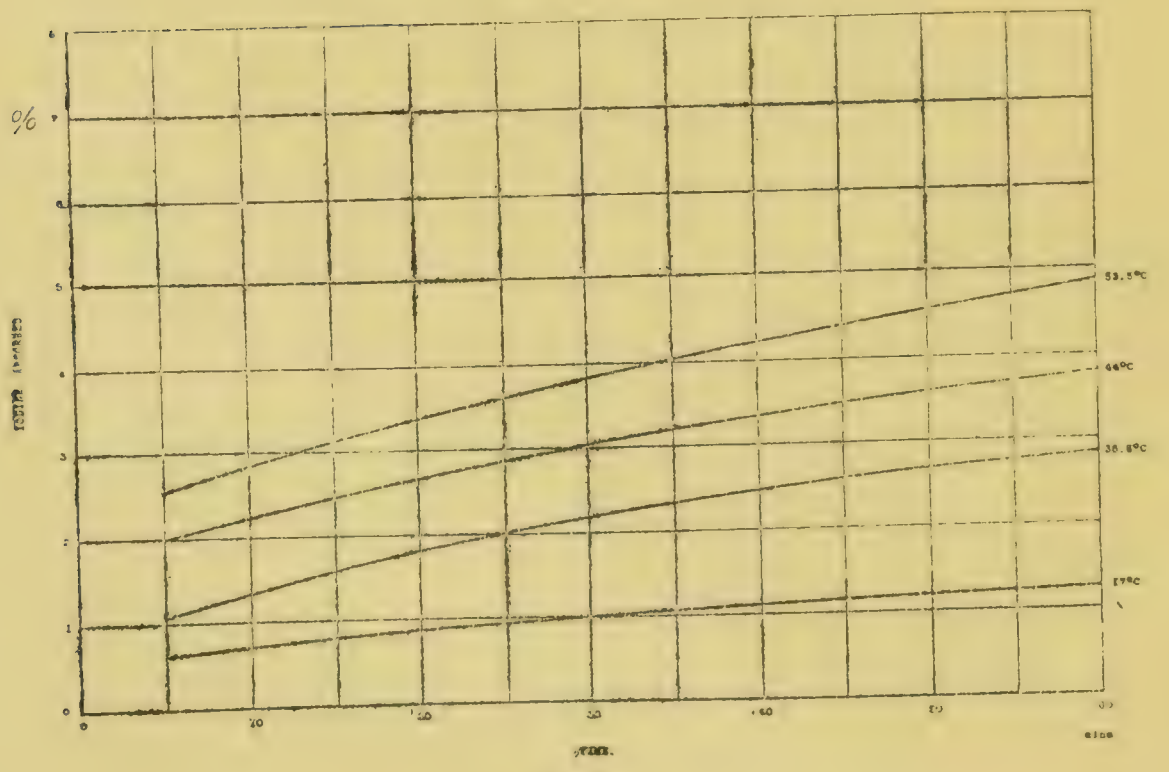


FIG. 5.

Iodine Absorption of Gelatine B. (Hard).

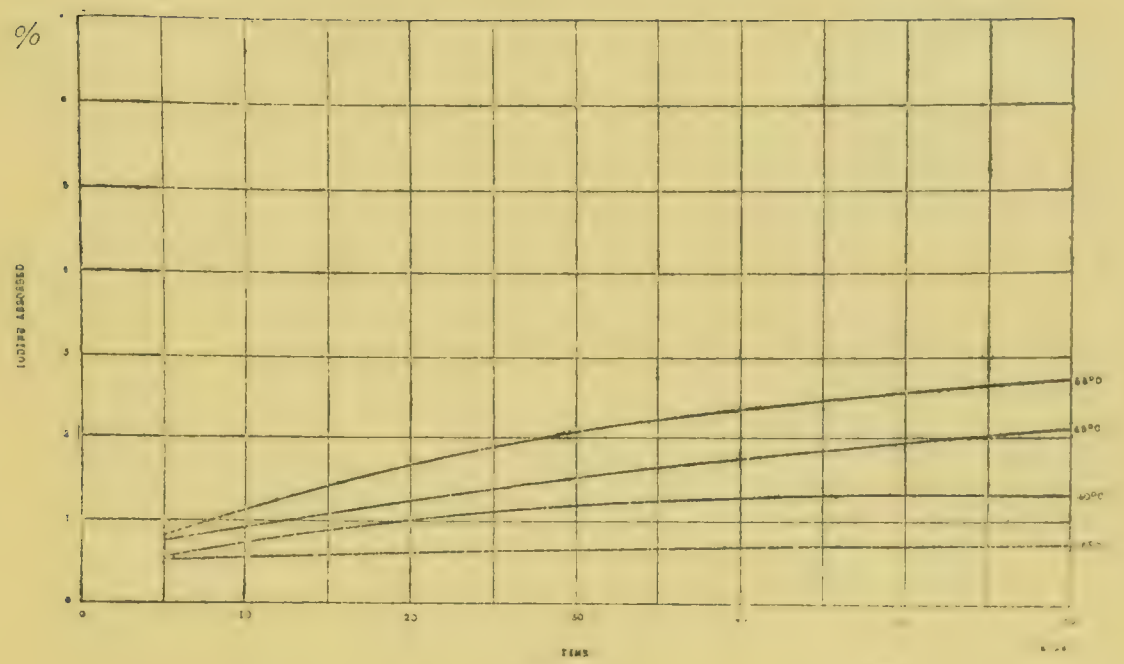


FIG. 6.
Iodine Absorption of Agar-Agar.

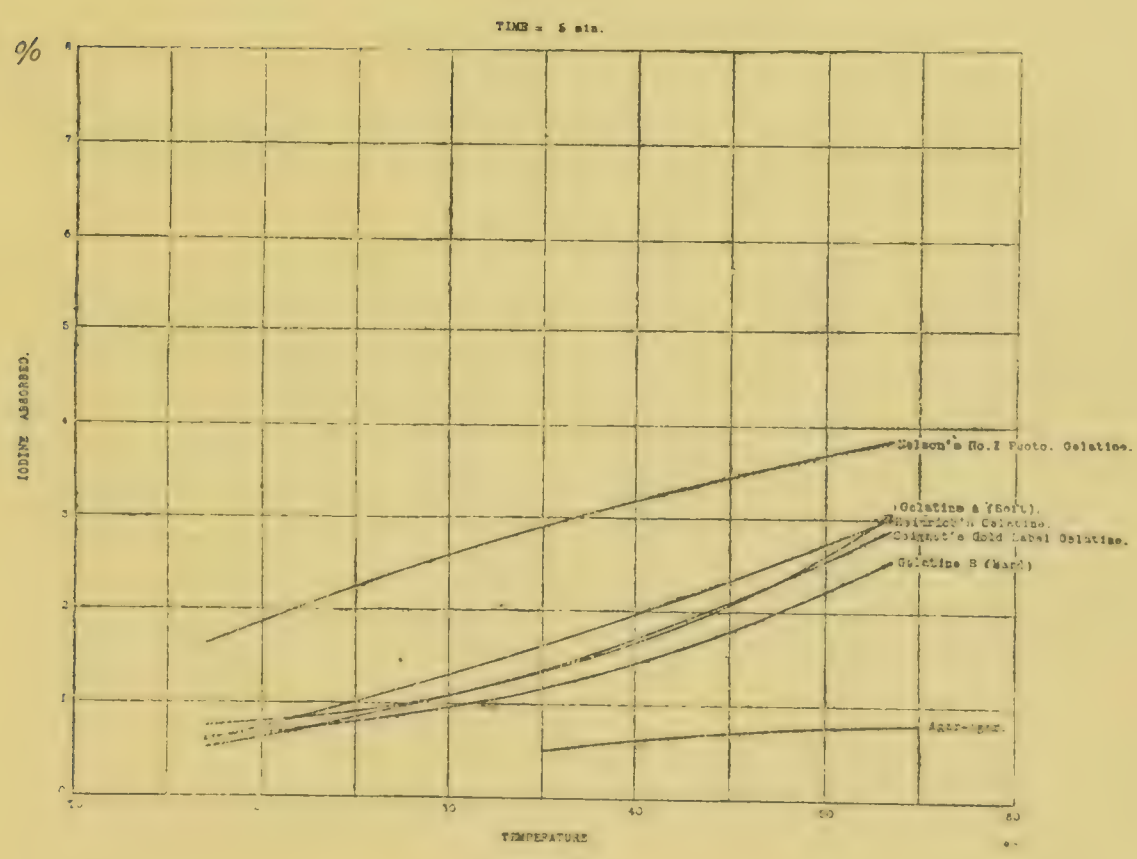


FIG. 7.
Iodine Absorption of Agar-Agar and Gelatine.

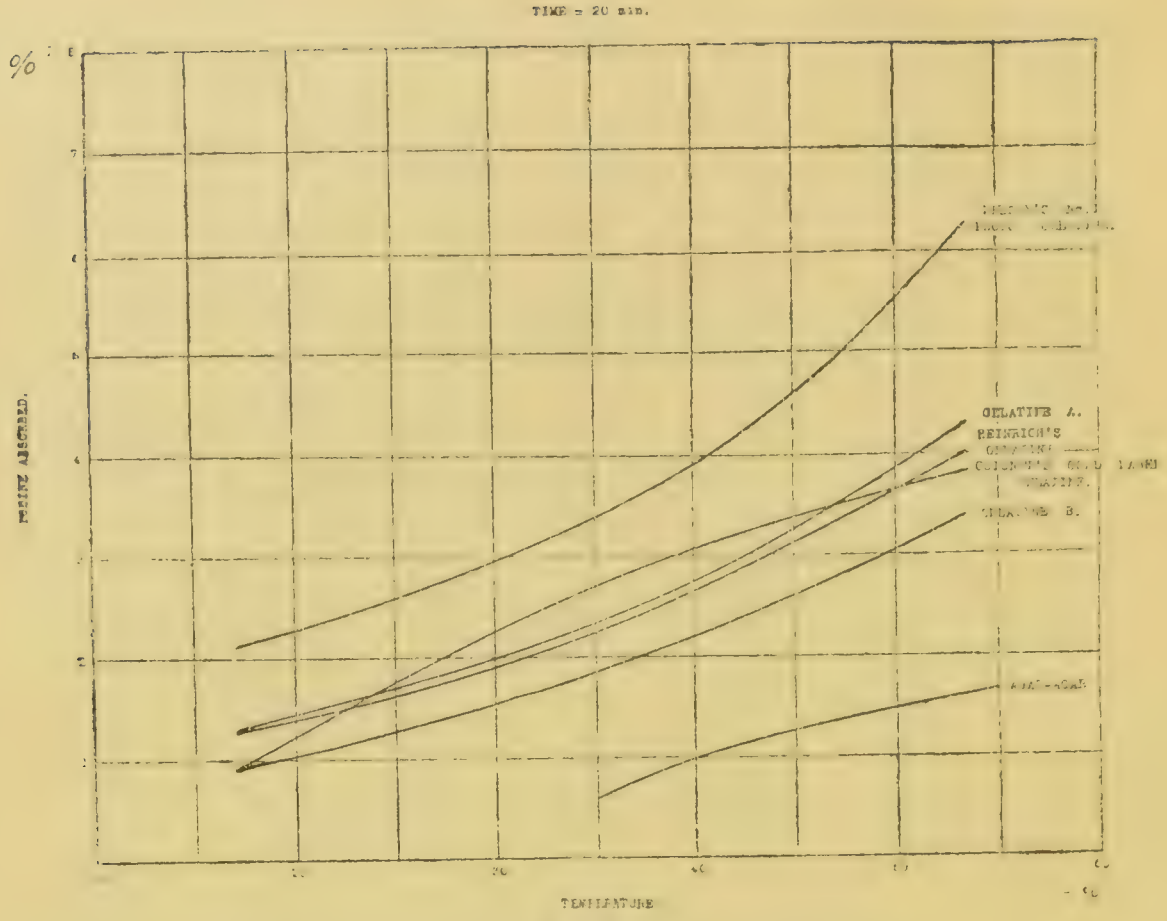


FIG. 8.
Iodine Absorption of Gelatine and Agar-Agar.

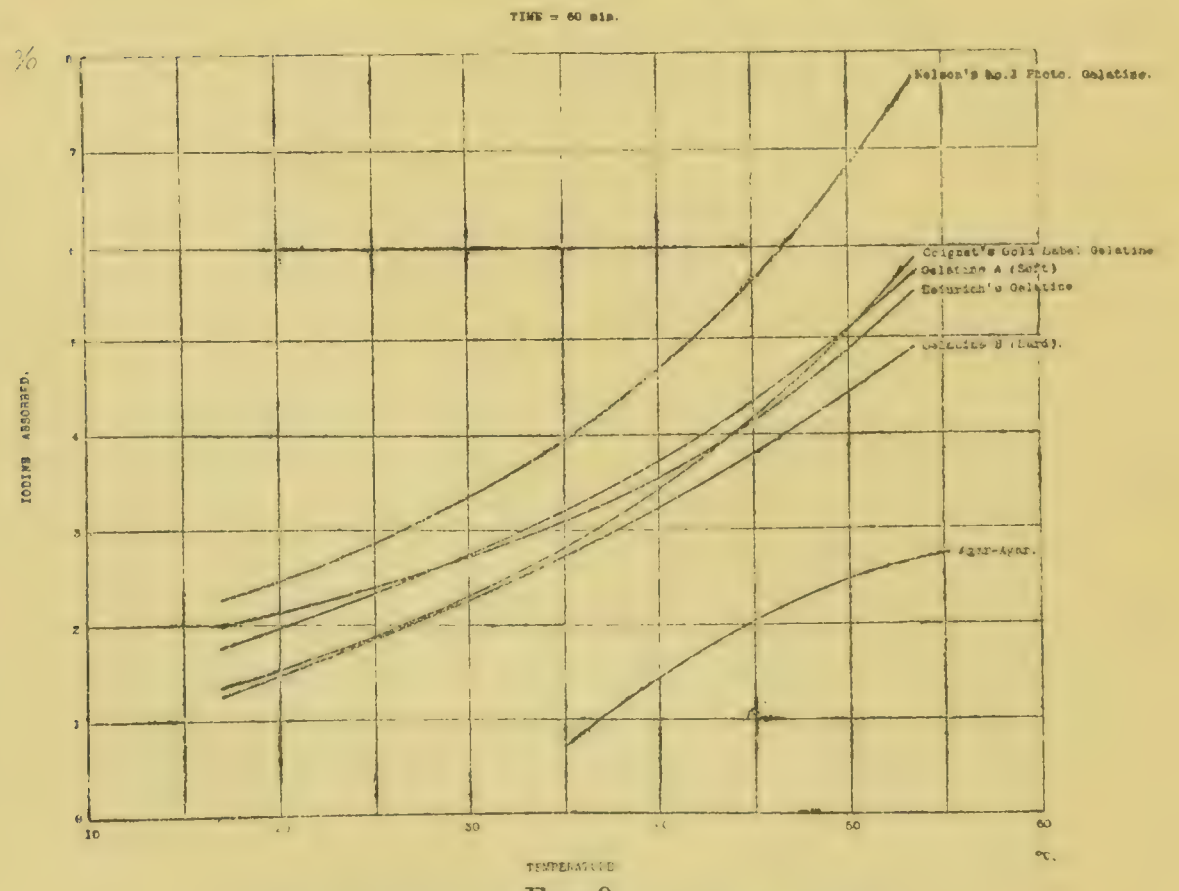


FIG. 9.
Iodine Absorption of Gelatine and Agar-Agar.

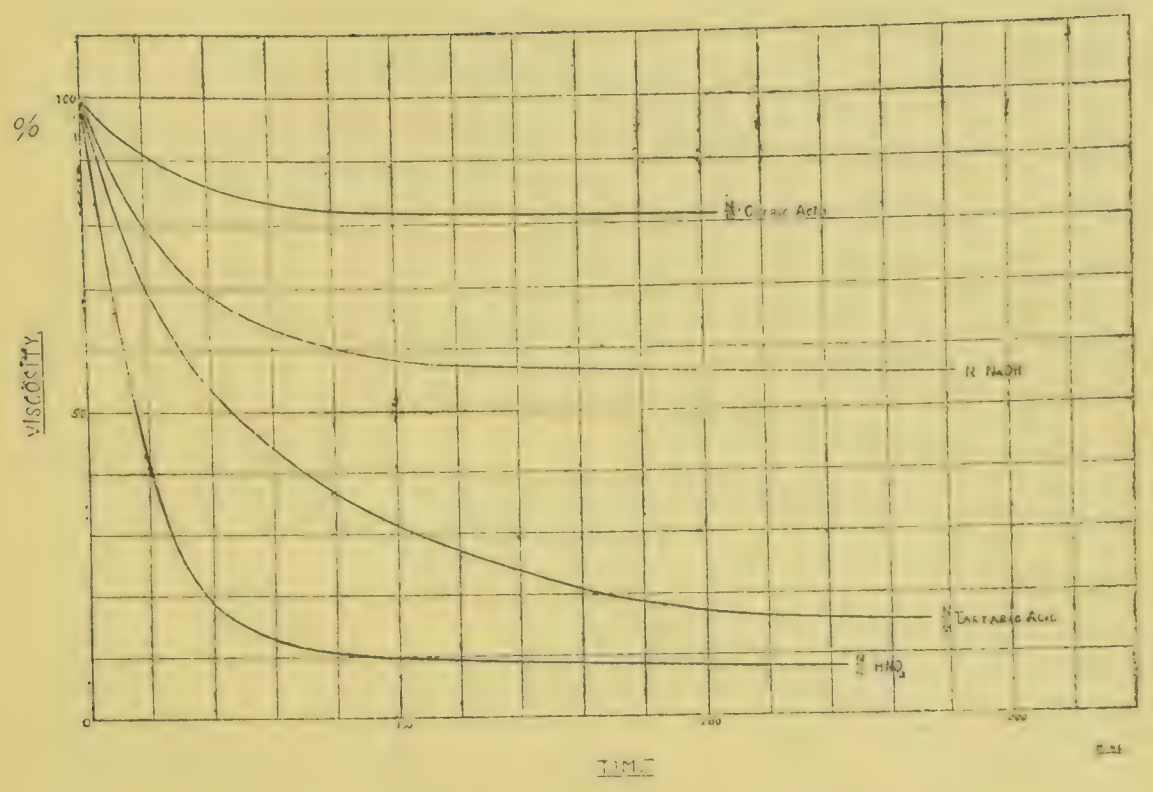


Fig. 10.
Effect of Reagents on Viscosity of Agar-Agar.

The Cooper Laboratory for Economic Research,
Watford.

Discussion.

Mr. R. Jahr said agar-agar has been tried for emulsions by himself as early as 1887 on the recommendation of Dr. J. Hinde, but without any success, the bromide of silver not being kept in suspension uniformly throughout the films and the plates giving considerable chemical fog. It seems as if the necessity of dissolving the agar at such a high temperature (90° C.) would prevent entirely its use for comparatively rapid negative emulsions. Perhaps there are several kinds of the material called agar-agar in the market, which might act differently.

Mr. W. H. Nuttall replied: It has already been admitted that the use of agar in the preparation of negatives is only in the experimental stage.

Nearly all workers with agar have experienced considerable difficulty in preparing emulsions with it, these being chiefly due to the

incorporation in the emulsion of substances which rapidly produce degelatinisation, and thus the precipitation of the halide.

Even when such hydrolysing agents are absent, an emulsion prepared by adding the alkali halide to the agar solution and then an aqueous solution of silver nitrate often is useless, as Mr. Jahr pointed out, owing to the precipitation and sedimentation of the halide. If, however, the silver nitrate is also mixed with agar, and this is added to another portion of agar containing the alkali halide, a perfectly creamy emulsion results.

The authors have noticed slight differences in different samples of agar, but these differences have not warranted the authors in attempting to classify agars from various sources.

Mr. F. F. Renwick said: Two other difficulties in connection with the use of agar-agar are its peculiar property of, so to speak, squeezing the water out of itself when in the gel state, thus giving a stronger gel than the one made and a watery solution which can be poured off, and secondly it will not mix with gelatine solutions permanently, but on setting and drying films of the mixture the agar separates from the gelatine in a granular form.

Major-Gen. Waterhouse said he had had a little experience with agar-agar, the first specimen he had used having been given him by Mr. Walter Woodbury, and came from Java. Agar was very commonly used in South-Eastern Asia for making an edible jelly or sweetmeat. He had tried it in photolithography and photocollotype, but had not found it of much use. For the latter purpose it gave a rough-grained thin film, inclined to be brittle. The solution, containing at the most about 2 per cent. even in boiling water, was thin, and if acids were used to increase the quantity dissolved, decomposition occurred and no advantage was gained. He had not tried it for emulsions, but had found the same difficulties in mixing it with silver nitrate and bromides as had been noticed by other speakers. He had, however, found that agar jelly formed a very convenient medium for electrochemical experiments.

On Gelatose and the cause of certain Variations in the Sensitiveness to Light of Mixtures of the Substance with Alkali Bichromates.

By Charles W. Gamble.

(ABSTRACT.)

The author has investigated the cause of certain variations in the affectability of gelatose when exposed to light in conjunction with an alkali bichromate.

When gelatine is submitted to the action of water or to dilute solutions of alkali or acid at a sufficiently elevated temperature hydrolytic cleavage takes place in the proteoid to an extent depending on the duration of the treatment. A similar effect is produced by the influence of certain putrefactive organisms and by proteolytic enzymes, as, for example, the digestive ferments, pepsin and trypsin.

The most obvious effect of the charge is the loss of one of the distinctive properties of the gelatine, viz., its ability to form a more or less elastic solid or jelly when associated with water, the changed gelatine forming a viscous solution, the mobility of which depends upon several factors, as the degree of cleavage, concentration, temperature, and to some extent the proportion of unchanged gelatine which may be present.

If gelatine be "dissolved" in water to a sufficient extent—say 10 grams of gelatine in 100 cc. of water—and the resulting solution be then allowed to cool to 15° C., the mass "gels." If the temperature be now raised, the gel passes into the liquid state. By suitable means the temperature constant at which this change occurs can be determined with accuracy, and the figure of value thus obtained is usually referred to as the "melting point." The converse of this, the "setting point," the temperature at which the liquid will gel, cannot be so readily obtained because of the time function, which, however, is of little moment in the determination of the previous named constant, the melting point.

The melting point of the jelly (which, within limits, is only slightly affected by concentration) varies primarily with the particular gelatine, but it also alters with the condition of the particular sample. Hydrolytic change very quickly depresses the

melting point, and the temperature value for this transition stage therefore forms an indication of the degree of cleavage which may have been brought about.

If the change be carried only partially the liquid will fail to gel at a certain temperature, but may do so if the mass be cooled further, frequently, however, only after a prolonged period. If the action has been carried sufficiently beyond this stage no jelly will be formed even at a low temperature; the property has been lost, and only a viscous liquid results. Further hydrolysis reduces the viscosity and eventually a very mobile liquid is produced.

If a solution of gelatine has been hydrolysed to an extent that it has lost its jelly-forming property there results the substance termed *gelatose*. By prolonged action the gelatose is converted into gelatine-peptone, and the resultant of the hydrolysis of the peptone is a complicated nature of amido-acids—glycine, leucin, aspartic and glutamic acids, and other bodies. It is desirable to avoid undue extension of the meaning to be applied to the terms "gelatose" and "peptone," and to regard them as groups of substances which behave in a certain manner, and not to assume that they represent simple entities. The substances gelatose and gelatine peptone correspond in many respects to the bodies which are produced by the hydrolysis of a simple proteid, to albumose and peptone, having at least this much in common that they behave towards certain reagents in a similar manner.

If to a solution of gelatose ammonium sulphate be added the body is precipitated. No precipitate is formed, however, by means of this reagent if the hydrolysis has been carried far enough to change the gelatose to gelatine peptone. With a solution of chromic acid similar differences are observed, the chromium compound producing a precipitate with gelatose, but none with peptone. If gelatose mixed with potassium bichromate be exposed in a dry condition to light, after a sufficient time there results such change that the substance is no longer soluble in water. In this respect it behaves like the parent body, gelatine. On the other hand, if peptone be similarly exposed, although the mixture darkens in colour, showing change, no insoluble substance remains on treating the exposed mass with water. No insoluble product is therefore formed with that portion of the hydrolised gelatine which is not precipitated by ammonium sulphate and chromic acid.

A form of gelatose which occurs in commerce is the well known

"fish glue," a viscous substance produced by the digestion of the bones and tissues of fish. This body is employed in photo-engraving processes in conjunction with alkali bichromates for the production of images on metal, which are eventually converted to "resists" against the action of etching mordants, and in such connection the gelatose has a large sphere of usefulness. Other forms of gelatose are obtainable, some attention having recently been given to the production of particular forms with a view to their subsequent use in photo-mechanical photography.

The various substances being hydrolytic products, produced on a commercial scale from substances varying in character, show, as might readily be expected, considerable differences, not only in comparison with each other, but also in different batches of the same preparation, and such differences are at times a source of irregularity in print-making for the production of engravers' resists. Inasmuch as the effect of unduly prolonged cleavage is to produce a substance of no value so far as concerns the production of an insoluble body with alkali bichromates, the formation of such should be avoided as far as is practicable. Further than this the presence of gelatine-peptone acts detrimentally by reducing the cohesion of the insolubilized gelatose, and so leads to the disintegration of the printed image.

The term sensitiveness as applied to the bichromated mixture has a meaning strictly defined, and is used only in lack of a more convenient term. Hitherto when attention has been directed to the elucidation of the changes which occur in light with mixtures of certain organic bodies and alkali bichromates the investigations have been confined principally to the changes produced in the metallic salt, and the condition of the organic substance has not received much attention. So far the problem of the changes which take place remains unsolved. The product of the hydrolysation of collogens, is gelatine in its different forms, which in turn yield other and related substances. The author endeavours to show that, so far as concerns the yielding of insoluble substances with chromium compounds, the affectability of such gelatinous bodies is confined to certain limits, conditioned by the degree of degradation.

Attention is drawn by the author to the possibility that cleavage changes in gelatine may play a considerable part in causing the differences which are found under varying conditions in the character of gelatine emulsions with silver salts.

The Action of Chromium Salts upon Gelatine.

By Charles W. Gamble.

(ABSTRACT.)

This subject first received serious attention at the hands of Eder, who in 1878, published the results of a comprehensive research,[1] which dealt not only with the chemical changes which occur when chromated mixtures are exposed to light, but also with the properties of such and their influence on the character of the results from a purely photographic aspect. The main conclusions deduced so far as concerns the nature of the chemical changes was that light exercises a reducing action upon the alkali bichromate in the presence of gelatine, producing chromium chromate, and finally chromium oxide, which reacts upon the bichromate, producing chromium chromate, and that eventually this was by further light action converted into chromium sesquioxide. The organic substance was, according to Eder, in part oxidized during the changes, and an insoluble body is formed by the union of the chromium chromate with the unaltered gelatine. The portion of the gelatine which acted as a reducing agent to the chromic acid was not found in the insoluble part. Eder's researches did not supply any exact information as to the nature of the compound of the gelatine with the chromium oxide—the insoluble substance. Although subsequent investigations have caused there to be same qualifications in the conclusions of Eder, they remain essentially unaltered.

It is well known that many bodies have the property of either rendering gelatine wholly insoluble in water or of merely raising the melting point of a gel of given concentration of gelatine. Such substances as produce complete insolubility are chromic acid, ferric chloride, formaldehyde, tannin, etc., while sodium, ammonium, or potassium alum raise the melting point of a gel, and produces the so-called "partial" insolubility. But chrome alum acts in either way according to the amount added. Small quantities produce partial insolubility, which insolubility is increased by an increase in the amount of the salt up to a certain point, when further additions produce a reverse action.[2] Because presumably of the acidity of the salt, Namias[3] has shown that a solution of any chromic salt which has an acid reaction has only a slight insolubilizing effect upon gelatine. Even a concentrated solution of ordinary pure chrome alum exercises only a slight influence upon sheets of gelatine

immersed in the liquid. But by treating the solution with ammonia, a basic salt of chromium is produced, and this exercises the maximum insolubilizing effect. Certain other chromic salts, such as the chloride acetate and tartrate, act in a similar manner, but the effect is not so pronounced. Namias points out that the insolubility produced by chromium salts has usually been considered to be due to a compound of the gelatine with chromic oxide, and he considers that the striking effect produced by chromic sulphate, as described, is due to the tendency of that body to be hydrolysed in solution into chromic oxide and sulphuric acid, but that little or no hydrolysis takes place with the other salts mentioned. The basic salt has an increased efficiency, because the absorption of chromic oxide from it by the gelatine does not produce so much pure acid. That the gelatine does abstract chromic oxide is shown by the fact that the solution gradually becomes acid. It is suggested that, inasmuch as the gelatine has a greenish tinge even after prolonged washing, the insoluble substance is a mixture of gelatine and a basic chromic sulphate rather than with pure chromic oxide.

Further light upon the work of Namias has been given by the investigations of MM. Lumière and Seyewetz,[4] who agree as to the formation of the basic salt by the treatment of chrome alum with an alkali. They show that basic chromic sulphate $Cr_2 (So_4)_2$, prepared after the manner of Recoura, is much more effective than the normal salt. This particular action of the basic salt is not, however, shown by a solution of chromium sesquioxide in alkali, and this difference is attributed to the presence of the alkali which they assume decomposes the compound formed between the chromic oxide and the gelatine. It has further been shown that when working with chrome alum, the insolubility produced by its addition to gelatine depends upon the concentration and the time which elapses after addition. The effect is thus progressive. The *minimum* quantity of chrome alum required to render gelatine resistant to the action of boiling water is 2 grams to 100 grams of gelatine, whatever the concentration of the gelatine solution. The maximum quantity of chrome alum that can be fixed by the same weight of gelatine is 21 grams, whatever the concentration. It was found by the previously mentioned authors that the insolubilizing action of the sulphate, sulphite, nitrate, chloride, fluoride, acetate, formate, citrate, tartrate, and lactate of chromium is less, the greater the amount of alkali required to produce a permanent precipitate of chromium hydroxide

in solutions containing equal weights of chromium, but otherwise is independent of the nature of the salt.

The gelatine which has been rendered insoluble by chrome alum appears on treatment with water to have an alkaline reaction, and before drying shows as an elastic transparent mass of a reddish violet colour with a greenish dichroism, or green, according to whether it has been rendered insoluble with the normal or the basic salt. By washing the gelatine in weakly alkaline water, the mass loses its transparency and becomes translucent, and with a stronger alkaline solution quite opaque, because of the precipitation of the oxide of chromium. If the insoluble gelatine is dried it becomes brilliant and of a deep green colour, is hard and brittle and easily reduced to powder. As to the actual state in which the chromium exists in the insoluble gelatine, the authors asked themselves (*a*) whether the chromium salt is fixed on the gelatine giving an additional product as in the case of a double salt, or (*b*) whether the gelatine playing the part of a weak acid decomposes the chromium salt giving a basic salt which combines or forms a compound of addition with the gelatine, or (*c*) whether the gelatine playing the part of a strong acid combines wholly with the Cr_2O_3 setting free all the acid combined with this substance. Experiment showed that in the case of chrome alum and chromium chloride the gelatine combined directly with the salt, for when gelatine was immersed in the solution even for so long a period as to withdraw nearly the whole of the chromium salt the solution showed on analysis precisely the same relation between the chromium and the acid as in the original salt. [Namias (*see ante*), that a solution of chromic sulphate became acid by immersing gelatine in it.] But by washing the mass with hot water the acid of the salt is gradually removed, and to prevent the acid solution so produced from acting upon the gelatine it is necessary to use weakly alkaline water to wash out the last traces of chrome alum before treating with boiling water. If the insoluble gelatine be treated with very dilute sulphuric acid (1:1000), the mass swells, and on boiling for a few seconds the Cr_2O_3 dissolves forming a green solution, the gelatine dissolving at the same time. If sufficient gelatine be present, a jelly is formed on cooling. This tends to show that the gelatine as such is not altered by its association with the chromium compound. If instead of sulphuric acid an alkali be used, the gelatine after swelling disintegrates and the Cr_2O_3 separates.

MM. Lumière and Seyewetz have shown that a given weight of gelatine fixes a practically constant quantity of chromium sesquioxide whatever be the nature of the chromium salt employed, and that this quantity varies between 3·3 and 3·5 grams per 100 grams of gelatine.

MM. Lumière and Seyewetz[5] presented to the Chemical Society of Paris in 1905 an account of the results of an investigation on the action of light on bichromated gelatine, they represent the initial change thus:—

$$K_2Cr_2O_7 = Cr_2O_3 + K_2O + 3O,$$

and accept the evidence of Eder's experiments that the gelatine is not oxidized by the oxygen shown as liberated. They found that chromic oxide is produced together with free potash, which forms with the excess of bichromate a neutral chromate. The quantity of this neutral chromate increases with the exposure, and that as the exposure is prolonged the reduction of the bichromate becomes slower. They also confirmed the formation of chromate of chrome as stated by Eder, but were not able to prove by analysis that its composition agreed with that of the chromate $Cr_2O_3CrO_3$, the compound always being deficient in chromic acid. They found that the quantity of chromium fixed by the gelatine insolubilized by light from a mixture of gelatine with bichromate is not constant as in the case of the direct insolubilisation with chromic salts (*see ante*). The amount varies with the concentration of the bichromate and the amount of light energy received. The amount of chromium sesquioxide retained was found to vary between ·39—10·0 grams per 100 grams of gelatine, but these quantities of chromium do not take account of the chromium chromate which may have become eliminated in the hot water washings necessary to get rid of the excess of unaltered potassium bichromate. On the whole the authors conclude that in the insolubilization produced by light at least three times as much chromium sesquioxide is retained as in the case of the gelatine rendered directly insoluble by chromic salts. Further the gelatine differs notably in composition from the directly insolubilized. The chromic oxide which it contains appears to be in two parts, the one fixed and corresponding to about 3·5 grams per 100 of gelatine which may be regarded as comparable to the chromic oxide held by the directly insolubilized gelatine, and the other variable with the duration of the exposure and arising from the reduction of the bichromate in light by the organic matter. It

is further noted that the quantity of chromic oxide held by the insolubilized gelatine increases with the duration of the exposure, but it is not directly proportionate, and the increase becomes smaller as the amount of neutral chromate which is formed increases. The decomposition of the excess bichromate by the chromic oxide with the formation of chromium chromate appears to be very partial.

In a further communication[6] the variations produced in the composition of bichromated gelatine when the potassium bichromate is replaced by other metallic bichromates and chromic acid. Taking the substances chromic acid and ammonium bichromate, it may be remarked that these bodies do not give rise to stable neutral chromates of much less sensitiveness to light than the initial bichromates, and it therefore was possible that prolonged light action might field insoluble gelatines containing more chromic oxide than given by potassium or sodium bichromates. This anticipation was realised, and it was found that in the presence of gelatine chromic acid and particularly ammonium bichromate are much more easily reduced than potassium bichromate. In the case of the ammonium salt there was retained by the gelatine an amount of Cr_2O_3, varying between 13·05 and 18·4 per cent., and with chromic acid 11·25—15·2 per cent. The quantities of Cr_2O_3 retained by gelatine in the case of other metallic bichromates was similar to the above, but in all instances the formation of chromium chromate was slight; at the same time it is very interesting to note that many of the insolubilized gelatines retained considerable quantities of the oxides of the particular metallic bichromate used. In the case of copper the quantity of CuO to Cr_2O_3 was 7·17 to 8·86 grams per 100 of gelatine, while with iron the insolubilized gelatine contained ferric oxide in considerable excess, the amounts being 12·4 grams of ferric oxide to ·93 grams of chromic oxide per 100 grams of gelatine. A further contribution to the study of the subject was made by the same authors in 1905, when the changes which take place spontaneously in the dark in bichromated gelatine were described.[7] The gelatine containing potassium bichromate was kept for varying terms (*a*) at ordinary temperatures and (*b*) at 120°C., and periodic examination was made until the gelatine was found to be quite insoluble in water at 80°C. After repeated washings the gelatine kept at ordinary temperature which had become insoluble was colourless, but that kept at 120°C. presented the same appearance as bichromated gelatine rendered insoluble by light action. In the

case of the gelatine kept at normal temperature complete insolubility was produced in 4½ months, while at 120°C. the same effect was obtained in six days, but there is this important difference, that while in the former case the gelatine does not *completely* resist the action of boiling water, in the latter instance it does. Examination of the insoluble gelatines showed that the sample obtained at normal temperature contained no chromic acid, and that the amount of chromic oxide varied between 0·67 per cent. for one month to 1·15 per cent. for 4½ months. In the case of the sample kept at 120°C. there was found to be an appreciable quantity at the end of one day. This body calculated to CrO_3 was ·54 per cent., and the quantity increased by keeping for six days to 2·54 per cent. When the gelatine was quite insoluble the chromic oxide varied between 8·68 per cent. for the first day to 20·59 per cent. on the sixth day.

In the gelatines thus examined there was no doubt a certain proportion of chromic oxide, which had no influence in the production of insolubility, and thereby results from the reduction of the bichromate of organic matter. It is further of interest to note that the gelatine rendered insoluble spontaneously contains much less chromic oxide than that rendered insoluble by light action.

REFERENCES.

1. *Eder, Josef M.* Ueber die Reactionen der Chromsäuren und der Chromate auf Gelatine, u.s.w.
   Wiener Photographische Gesellschaft, 1878. *Photographische Correspondenz.* Wien An account of the communication, which is very lengthy, appears in the *Photographic News*, 1878, 1879, p. 172, *et seq.*
2. *MM. Lumière et Seyewetz.* Sur la réaction acide des aluns et l'influence de cette acidité sur l'insolubilisation de la gélatine dans le cas de l'alun de chrome. *Bulletin de la Société Chimique de Paris*, 3e série, t. 27, p. 1,073 : (1902).
3. *Namias, R.* Azione sulla Gelatina dei composti varidi cromo e sua importanza practica in fotografica. *Bull. Soc. Fot. Ital.* 14 (1902), 268, and *Photographische Correspondenz*, 39, 446.
4. *MM. Lumière et Seyewetz.* Sur la composition de la gélatine insolubilisée par les sels de sesquioxyde de chrome et la théorie de l'action de la lumière sur la gélatine additionnée de chromates métalliques. *Bulletin de la Société Chimique de Paris*, t. 29, p. 1,077 (1903).
5. *MM. Lumière et Seyewetz.* Sur la composition de la gélatine imprégnée de bichromate de potassium insolubilisée par la lumière et sur la théorie de cette insolubilisation. *Bulletin de la Société Chimique de Paris*, 1905, III., 33 1032—1040.
6. *MM. Lumière et Seyewetz.* Sur la composition de la gélatine insolubilisée par la lumière en présence de l'acide chromique et des principaux bichromates métalliques. *Bulletin de la Société Française de Photographie*, X. 21, 461.
7. *MM. Lumière et Seyewetz.* Sur la composition de la gélatine insolubilisée par la lumière en présence de l'acide chromique et des principaux bichromates métalliques. *Bulletin de la Société Chimique de Paris*, t. 29, p. 1,077 (1903).

Photographic Films of Nitro-Cellulose.

By Henry M. Reichenbach, *Yonkers, N.Y.*

The beginning of the manufacture in the United States of gelatino-bromide films on a nitro-cellulose base, and which are so widely used throughout the world by amateur photographers, was the result of accidental knowledge acquired by the writer that wood alcohol would dissolve a large proportion of collodion cotton.

It was in the early days when celluloid or zapon varnishes or lacquers were being substituted for the resinous or lac solutions used in the coating of metals to preserve their lustre and prevent the tarnishing in handling.

The price demanded by the manufacturers of these lacquers was very high, and the people making the cameras for Eastman at that time, desired a cheaper product for coating the brass work on photographic apparatus. This cheaper product I was attempting to produce for them.

I had been engaged some two years as chemist of the Eastman Dry Plate and Film Company in improving and perfecting their products, gelatino-bromide plates, bromide paper, negative paper and stripping films. The negative paper and stripping film were the forerunners of the transparent film.

The Kodak had been launched and the stripping film with which it was loaded proved inimical to the wide sale of this instrument, on account of the troublesome transfer processes involved in the production of a printable negative.

The accidental knowledge of the fact that a concentrated solution of pyroxylin could be obtained by means of so cheap a solvent as wood alcohol presented a possible means for the production of the necessary transparent support for the emulsion in place of the paper then employed. My knowledge of the various solvents of nitro-cellulose was limited to the information to be obtained from the usual works of chemical reference at that period. These solvents were ether and alcohol, acetic ether, glacial acetic acid, none of which seemed adapted to the commercial manufacture of a satisfactory base, their cost was also prohibitive of their employment.

A few weeks of experimenting and research in special lines of

manufacturing resulted in the production of a satisfactory support. Detailed account of the various experiments is not interesting. This support consisted essentially of camphor and pyroxylin deposited by spreading on glass plates a solution of them in wood alcohol, amyl alcohol and amyl acetate, and the evaporation of this solvent. This process was the subject of a patent granted the writer in 1889. The camphor gave flexibility to the product; a larger proportion than necessary for this purpose was used inasmuch as it made a cheaper product. The basic cost of camphor at that time was less than one-half the cost of pyroxylin, a condition which has been reversed, and the films of the present therefore contain much less camphor. It was found that a reduction in the percentage of camphor used required a corresponding reduction in the proportion of amyl alcohol.

The process now seems simple enough with our wider knowledge of the various solvents of pyroxylin and their individual action in the production of a suitable base for photographic emulsions. Much difficulty was experienced in obtaining proper and uniform material and in gaining the experience necessary to the production of a satisfactory product, many new mechanical appliances were devised.

The first films offered commercially were made upon glass tables composed of several plates joined together. These tables were 50 feet long and 31 inches wide, and single pieces of film were produced thereon approximately of these dimensions. From films made on these tables began the motion picture industry as well as that of the Kodak.

Since my original experiments I have determined that the film may be made upon other supports than glass. Aluminium answers admirably.

The glass table process has been superseded in the United States by the use of revolving metallic drums and belts on which the support is made, and this support is coated with the sensitive emulsion after removal from the surface on which it is formed. When glass tables were used the pyroxylin solution was applied to the surface and dried and then coated with the sensitive emulsion which in turn was dried and the completed film stripped from the surface. This method, though used for many years, was not entirely satisfactory on account of the exposure of the surface to foreign matter in the surrounding air and the marking of the sensitive surface by the static electric discharges taking place during the stripping or separation from the glass. I have seen sparks or discharges more than a foot in length

developed by rapid stripping. The "tree"-like markings on the film after development were the source of much speculation on the part of early users of films. These were later largely eliminated by keeping a sharp wooden edge covered with a dampened linen cloth close to the point of separation of the film from the glass.

As to the constitution of a satisfactory flexible and transparent base for photographic emulsions, pyroxylin or pyroxylin and camphor in my experience are best. Pyroxylin alone seems too resilient. The only objection to pyroxylin and camphor is the shrinkage of the film on the edges causing curling, due to the evaporation of the camphor. The camphor exercises no injurious action upon the sensitive emulsion as is often claimed; exhaustive experiments have proven this. I have digested gelatino-bromide emulsion for hours with large quantities of camphor in a fine state of division without appreciable effect upon the emulsions.

The films made by the Eastman Company up to 1892 under my supervision were never dated, and with few exceptions kept perfectly for years under extreme climate conditions. These films all contained camphor in large proportion. The inflammable character of nitro-cellulose compounds is the greatest objection to them, and the substitution of aceto-cellulose has been suggested. My experiments in this direction have not proven satisfactory, likewise attempts at denitrification.

The ideal film support has yet to be invented, a new substance for its production discovered.

Sur un important perfectionnement apporté, par M. Danesi, aux méthodes et aux machines pour la photocollographie.

Par Prof. R. Namias.

Le procédé de photocollographie ou de phototype est sans doute un des plus importante procédés de réproduction photomécanique. Mais on peut dire que, depuis sa découverte faite par Poitevin il y a bien d'années, jusqu'aujourd'hui il n'a reçu que peu de perfectionnements.

Si les machines rapides pour l'impression des planches photo-

collographiques ont permis de rendre assez économique le tirage, on ne peut pas affirmer que les résultats ayent subi une amélioration par l'introduction de ces machines.

On remarque bien de fois dans les impressions photocollographiques un manque d'effets par insuffisance d'encre à laquelle est difficile à remédier. En effet si on cherche par une couche plus épaisse de gélatine d'obtenir des creux plus profonds on se trouve en présence de la difficulté d'encrer bien les planches dans la profondités des creux et surtout d'imprimer sur papier ces planches sans une pression trop forte à laquelle le risque de la cassure de la plaque est considérable.

Mons. Giulio Danesi de la grande Maison photomécanique de Rome (auquel on doit aussi une machine à graver qui fonctionne d'une manière parfaite et qui a été adoptée par plusieurs maisons d'Italie et de l'étranger) vient de porter au procédé de photocollographie un perfectionnement qui me semble mériter toute l'attention de ceux qui s'intéressent des questions photomécaniques.

A la suite d'un grande nombre de recherches il est réussi à substituer à la planche en verre rigide et cassable, une feuille d'aluminium. On comprend qu'il a du vaincre assez de difficultés pour obtenir sur ce support métallique flexible une couche régulière et adhérente. La feuille d'aluminium sur laquelle on forme l'image de la même manière comme sur planche en verre, est adaptée au *cylindre* d'une machine rotative spéciale étudiée par M. Danesi et destinée à rendre possible l'impression rotative des images photocollographiques.

Je vous présente ici une réproduction photographique de cette machine. On y voit plusieurs rouleaux dont quelques-uns sont déstinés à l'encrage et d'autres au mouillage de la planche. Une rationnelle disposition assure un étendage parfait de l'encre.

Avec cette machine rotative la production est augmentée d'une manière très considérable, et on évite en outre tout inconvénient de cassure. Mais le principal avantage de cette heureuse création de M. Danesi consiste dans la possibilité de faire une double impression sur la même feuille du papier en augmentant beaucoup de cette manière la richesse de tons et l'effet de l'image.

La disposition imaginée est telle que l'exact repérage des deux impressions est assuré.

Malgré l'avantage considérable de cette double impression pour les résultats on a encore un tirage plus que double de celui qu'on

obtient avec les machines ordinaires pour l'impression photocollographique.

Je vous présent ici quelques résultats qui confirment les affirmations que j'ai fait. La richesse de tons qu'on obtient avec cette double impression est telle qu'on peut comparer ces épreuves à celles qu'on obtient par le procédé énormement plus coûteux d'héliogravure en creux.

Deux de ces épreuves montrent la différence qu'il y a entre les résultats obtenus par la simple et la double impression.

Congrès International de Photographie, Bruxelles, 1910.

Communication de MM. R. Namias et L. P. Clerc.

La Commission Permanente des Congrès Internationaux de Photographie organise un Cinquième Congrès International, qui se tiendra en juiliet 1910 à Bruxelles, pendant l'Exposition universelle.

La Commission Permanente serait heureuse d'accueillir le concours du plus grand nombre possible de techniciens pour assurer l'intérêt de cette manifestation. Trois sections principales sont dès à présent prévues, réservées respectivement aux questions scientifiques (sensitométrie, chimie des opérations photographiques), aux questions pratiques, et aux questions de documentation (documentations judiciaire, topographique, etc.).

Nous serions particulièrement désireux de voir des comités locaux se former dans les principaux pays, comités existant déjà en Belgique, en France et en Italie, et qui dans les autres pays pourraient se constituer autour des membres de la Commission Permanente.

Tous renseignements pourront d'ailleurs être obtenus sur demande au Secrétariat de la Commission Permanente des Congrès Internationaux de Photographie, 51 rue de Clichy, à Paris.

Présentation d'un album d'illustrations de Messnai et Reggio, Calabria.

Faite par Prof. R. Namias.

à nom de la Società Fotografica Italiana.

A la séance du 1 juin Mons. le Prof. R. Namias de Milan présenta un album contenant un grand nombre d'illustrations des malheureux pays Messina et Reggio, Calabria, avant et après l'horrible cataclysme.

Il fait remarquer que ces illustrations sont destinées à constituer la Monografia Illustrata di Messina e Reggio qui va être accomplie par l'œuvre de la Società Fotografica Italiana de Florence.

Cette Monographie contiendra à peu près 600 photographies, vues, monuments, trésors artistiques etc., avant et après le tremblement de terre ; photographies des types de ces pays, scènes de sauvetage ; photographies des navires des différentes nations qui ont apportées concours à ces sauvetages ; sismogrammes d'observatoires sismographiques de tout le monde, plans topographiques et hydrographiques de ces pays etc.

L'ouvrage contiendra des articles de personnages éminents d'Italie, et sera publiée en quatre langues. La vente sera faite à profit de l'institution pour les orphelins que le désastre a laissé sans moyens.

Le Prof. Namias fait remarquer en outre que cet ouvrage représentera le plus important ouvrage de documentation photographique qu'ait été jamais faite et il signale toute l'importance qu'elle est destinée à avoir pour l'histoire et pour les habitants de ces pays.

Aids to Photo-Micrography with Radiations of Short Wave-length.

By W. N. Hartley, D.Sc., F.R.S., *Royal College of Science, Dublin.*

Three years ago Mr. Walter T. Swingle, of the United States Department of Agriculture, consulted me on the diactinic properties of metastyrol, a polymerised form of phenyl-ethylene. He had found it to be a valuable medium in which to mount microscopic preparations because it permitted the use of the *a*-monobromnaphthalene as an immersion fluid with Abbé's lens of 1·6 numerical aperture. The great transparency of metastyrol and its resistance to the action of heat led Mr. Swingle to believe in the possibility of using it for the construction of a new type of microscope objective, available both as a visual instrument and as a photographic lens of still higher resolving power. It became necessary, therefore, to ascertain what rays it would freely transmit, and by what particular ray the finest definition and resolving power could be obtained by photography. A further important question arose as to the most suitable solvent, both as regards refractive index and volatility, which might serve for the preparation of an immersion fluid by being brought up to the required point of refraction without difficulty.

Selecting the heaviest *uviol* flint of Schott's make as a suitable glass, inasmuch as thin plates are reputed to be diactinic to about λ 2800, we may restrict the investigation in the first instance to rays less refrangible than this. It must be understood that carbon disulphide, on account of its high refractive index and great absorption of the ultra-violet rays, is not suitable as a solvent. After making a series of experiments I recommended chloroform for dissolving metastyrol, and one of the spark lines of cadmium such as λ 2748, that of magnesium λ 2852, or a silver line λ 3280. The best effect in photo-micrography is to be obtained by selecting a sharply-defined, isolated, narrow line of great emissive intensity and short wave-length. Mr. Swingle informed me that he had adopted my suggestion of using chloroform and obtained beautiful specimens mounted in metastyrol. The transparency of the preparations to the cadmium and magnesium rays had been tested, but a sharp falling off was observed between the magnesium line λ 2800 and the cadmium λ 2750; in fact, though the magnesium rays passed through the preparation they were

perceptibly weakened. The cadmium ray cast an almost black shadow and caused fogging of the plate, by reason of the fluorescence of the metastyrol, but several photographs had been taken with Zeiss monochromatic objectives, which were fairly successful when the magnesium ray was used. The fluorescence of the metastyrol is caused by those strong rays of cadmium which are more refrangible than λ 2748, and it is very desirable that the action of all such rays should be suppressed by an absorbing layer or by a mechanical screen, or be diverted by refraction from entering the fluorescent medium. Rock crystal when examined with the light of the cadmium spark has a pale violet fluorescence, and fused quartz a blue fluorescence. Thin slips of uviol glass for use as supports for microscope preparations were found to be quite as diactinic as quartz, but they showed a greenish-blue fluorescence. They transmitted with undiminished intensity all the lines of cadmium as far as λ 2245. If specimens are mounted on, and covered with any one of these substances, there is a possibility of prolonged exposures causing a fogging of the photographic plate, as was found in the case of preparations mounted in metastyrol. The screening of the object from rays capable of causing fluorescence is an important condition for the production of sharply-defined photographs.

A knowledge of the transparency of various organic substances to ultra-violet light becomes of practical importance in relation to biological research, by facilitating the application of the new monochromatic objectives. On this account I have renewed my examination of some of these substances, recording their diactinic properties, boiling points, refraction indices, and also their facility in dissolving such substances as metastyrol. It will be understood that the object to be obtained is photography by transmitted rays, for the differentiation of tissues and observations on structure, and not for observing by means of diffracted rays, as in Siedentopf's recent improvements (1907) in ultra-microscopy, for an account of which I am indebted to the firm of Carl Zeiss, London.

After careful consideration of their properties, many substances were rejected as being unsuitable as solvents, but a selection of the best was made, and each liquid was submitted to a complete examination. One of the difficulties encountered arose from the sparing solubility of metastyrol as compared with that of the usual resinous mounting materials, and also in the too free volatility of some good solvent liquids.

Taking into account the layer of material under the cover glass and that on its surface acting as the immersion fluid, we may reckon 5 to 10 μ as the maximum thickness for the penetration of the rays; it was therefore decided to test solutions through 10 mm. as a maximum, then to evaporate successive quantities of 1 cc. of the strongest solution of metastyrol on quartz glass and photograph through these until a sufficient quantity of, say, that contained in 10 cc. of the solution had been examined.

The screen.—As a fluid screen for intercepting the more refrangible rays and preventing difficulties arising from fluorescence, the following liquids were judged* to be the most convenient:—

1. A solution of 1 gr. of quinine in 1 litre of normal sulphuric acid; this intercepts all rays more refrangible than λ 2700, when a layer of 5 mm. to 10 mm. thick is used in a quartz cell. The rays transmitted and absorbed by 5 mm. and 4 mm. of this solution have been measured and are given below. There is a strong band of absorption in the ultra-violet.

Rays transmitted from Cd 1, λ 6439·3 to a tin line λ 3801·2.

An *absorption band* extends from λ 3801·2 to Cd 16, λ 2837·0.

Rays transmitted beyond the band lie between Cd 16, λ 2837·0 and λ 2643·8 a tin line.

All rays beyond λ 2643·8 are absorbed completely.

The line Cd 17, λ 2748·7 is the only line of the cadmium spectrum transmitted with *undiminished intensity* through 4 mm. and 5 mm. of this solution, and with 10 mm. it is the only line transmitted which is more refrangible than λ 3940·4.

2. A solution of quinoline in alcohol containing 1·3 grs. per litre transmits all rays strongly as far as a tin line λ 3175·1 through 2, 3, 4 and 5 mm. A lead line λ 3243·0 is transmitted through 10 mm. of the solution, with total absorption beyond. These solutions are colourless and can be used for the visual rays when it is desired to suppress light causing fluorescence. In the case of quinine the strong absorption band between λ 3800 and λ 2748·7 admits of the isolation of this cadmium line by the use of a coloured solution which absorbs the visual rays less refrangible than λ 3940·4. The application of a dye for this purpose is a subject for future investigation.

3. A solution of pyridine in alcohol containing 4 grs. per litre transmits all rays to λ 2748·7 through 5, 4, 3 and 2 mm. thickness, and to λ 2742 through 2 mm. and 1 mm., with total absorption beyond.

---

* The Absorption Spectra of the Alkaloids. Hartley. Phil. Trans. Part II, 1885. pp. 471-521.

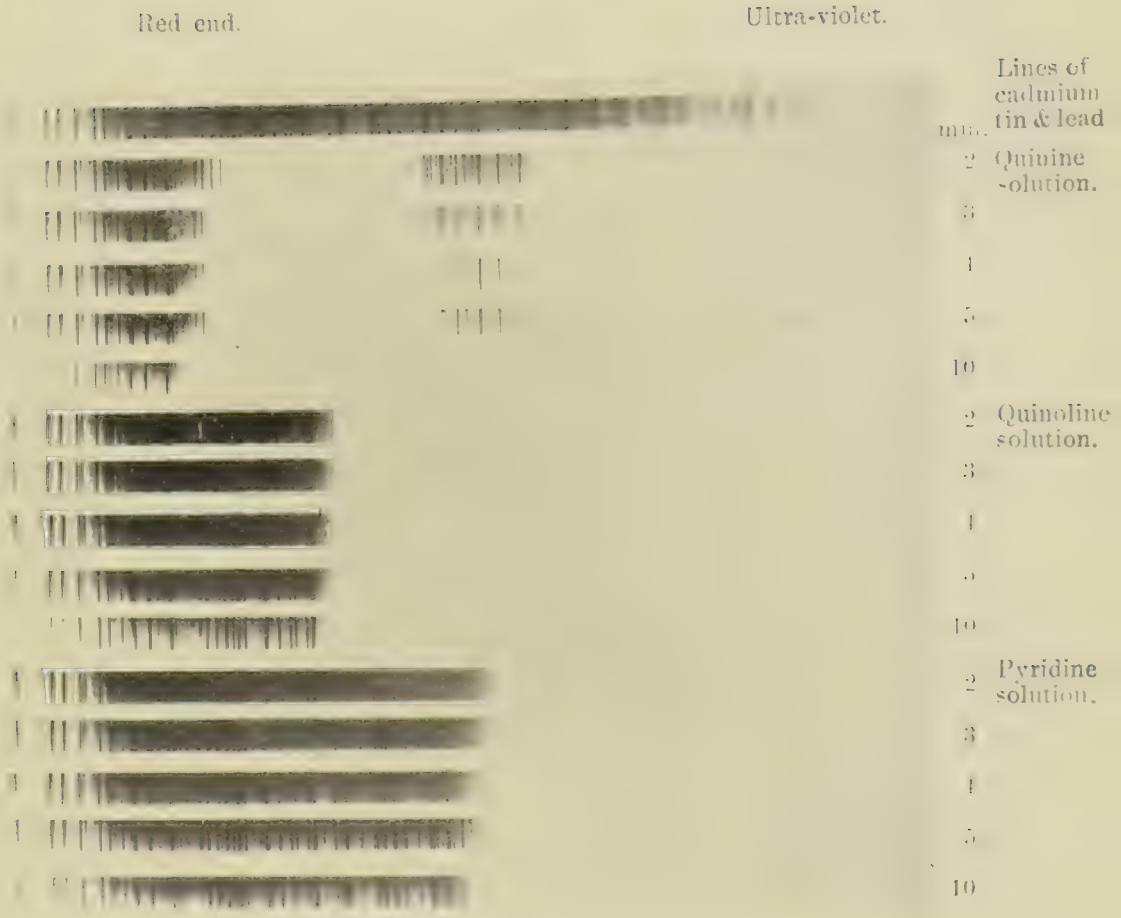


FIG. 1.

Absorption spectra of solutions of—

1. Quinine sulphate in alcohol.
2. Quinoline in alcohol.
3. Pyridine in alcohol.

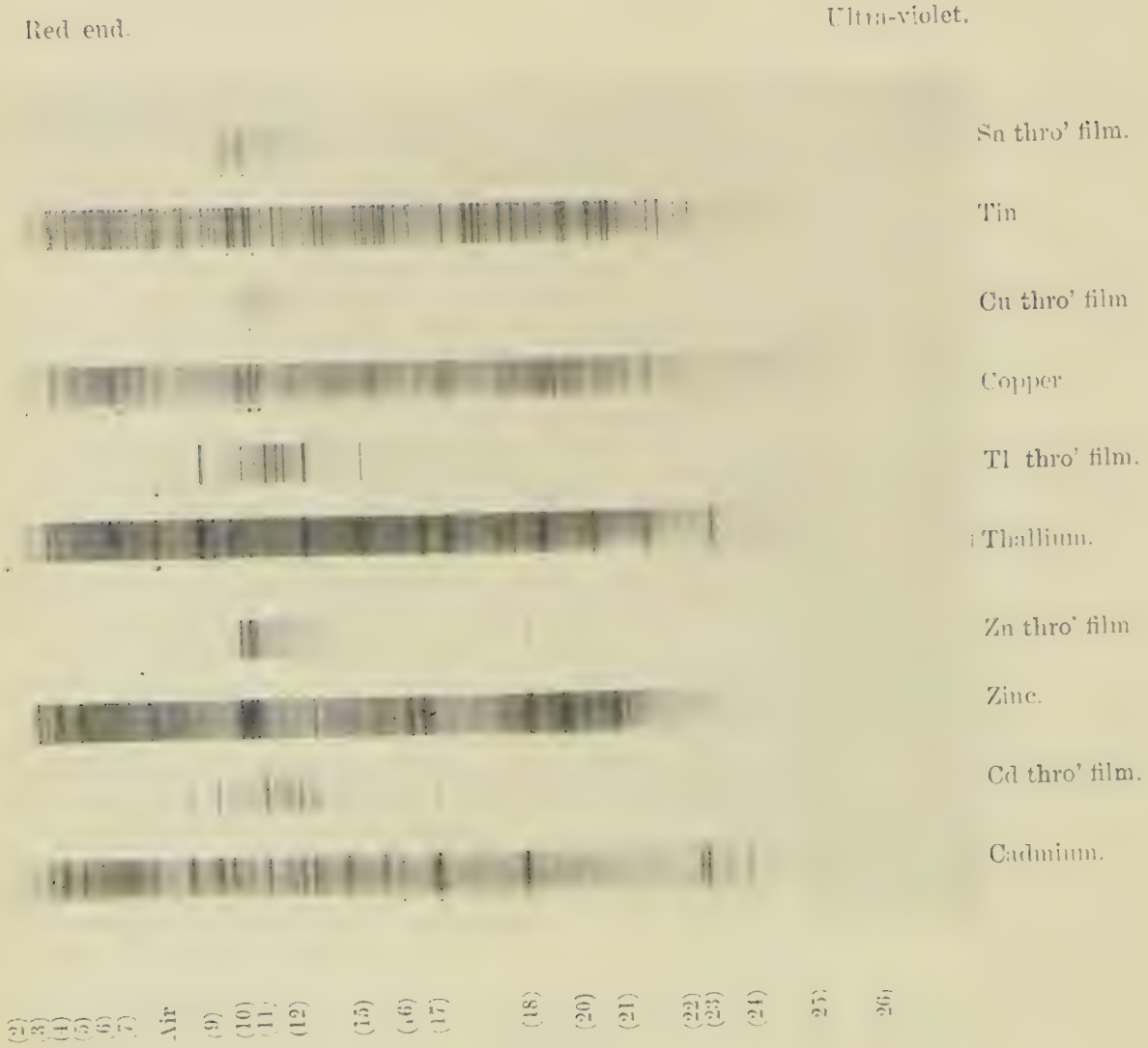


FIG. 2.

Spark spectra of different metals through silver film deposited upon quartz.

The relative opacity of films of silver.—If a plate of quartz or uviol glass has a film of silver deposited upon one surface, it may be rendered very nearly opaque to white light and yet transmit a band of rays lying between the solar lines P and S, $\lambda\lambda$ 3360 and 3100. With such a screen it should be possible to dispense with a prism for isolating a single ray. But it has been found that films deposited by different processes greatly differ in opacity—those which are the most opaque transmit a little brown light (probably a mixture of red and green rays), others transmit blue rays, and the ultra-violet somewhat freely.

The monochromatic light.—As a source of light only spark spectra have been available, but these have been simplified and made similar in constitution to arc spectra, by passing the current through a Hemsalech self-induction coil. In the following list it must be understood that the wave-lengths given are of lines common to the arc and spark, unless otherwise stated.

List of Lines common to arc and spark, lying between wave lengths 3360 *and* 3100.

Abbreviations—*r* reversed, *b* broad, *s* sharp.

	λ		*Intensity*
Cadmium No. 12	3261·2	arc	10 *r*
„ „ 13	3133·3	„	8 *b*
„ „ 16	2837·0	„	8 *r*
„ „ 17	2748·7	„	10 *s*
Zinc triplet	3345·1	„	10 *r*
„	3303·0	„	8 *r*
„	3282·4	„	8 *r*
Thallium	3229·4	„	10 *r*
Copper	3274·1	„	10 *r*
„	3247·6	„	10 *r*
Tin	3175·1	„	8 *r*
Mercury, a pair	3147·7 3131·9	spark	
Mercury, a single line	2967·4	vacuum tube and arc.	

The last mercury line is very intense in the spark. The mercury lines are quoted because it is possible to obtain them by using the mercury-vapour arc lamp with uviol glass or quartz tube. There is a powerful air line which is always to be seen in spark spectra when photographed from condensed sparks with no self-induction in circuit. Aluminium electrodes exhibit it very well. On careful examination it appears that there is another one close to it but a little more refrangible; the wave-lengths of the two are 3331·83 and 3329·62 (Hartley and Adeney). It might be convenient to use this line.

On the rays transmitted by silver screens.—As already mentioned, deposits of silver on plates of quartz differed in density and diactinic quality. It was therefore found desirable to measure the rays transmitted in each case, and also to examine the silver reduced on a celluloid film after exposure and development in the usual manner, the celluloid film being also examined.

	Exposure. seconds.	Rays transmitted.
I.—Clear celluloid	30	All to λ 2800
Exposed silver film on celluloid developed with quinol and caustic alkali.	15	λ 3180 to λ 3080
	30	λ 3235 to λ 3070
	15	Sn line λ 3175·1
	30	Sn line λ 3175·1 and Cd λ 3261·2
II.—Silver deposited by Edser and Stanfield's process, on quartz. Brown light transmitted. Reducing agent, milk sugar.	15	λ 3270 to λ 3110
	30	λ 3290 to λ 3100
	60	λ 3300 to λ 3080
	30	Lines, Cd 3261·2 and
	60	Sn 3175·1
	90	The same
III.—Silver deposited on quartz by Martin's process. Blue light transmitted. Reducing agent, sugar candy and tartaric acid.	60	Lines very strong. Cadmium (9) 3613·0, 3610·7. (10) 3467·8 and 3466·3. (11) 3403·7. (12) 3261·2, 3252·6, 3250·5, and (15) 2980·8.
	60	Lines of thallium. Very strong, λ λ 3775·9, 3529·6, 3519·4 and 3091·9. In every case the portion of spectrum most strongly transmitted lay between λ 3500 and λ 3050.

The photographic plate No. 50, Fig. 2, shows the rays belonging to each metal transmitted through the silver film III., which is transparent to blue rays, and it also shows the relative intensities of the lines, with an exposure of one minute. It is obvious, however, that a film which is very transparent can be of little service as a screen, and therefore the more opaque deposit II., which transmits brown light, is the more efficient. This transmits the line of cadmium, λ 3261·2 and that of tin, λ 3175·1. It will also transmit the thallium line, λ 3091·9.

The solvents of metastyrol and the properties of solutions of this substance.—Having examined many substances likely to prove useful as solvents, I have made a selection of those that are most suitable as regards diactinic properties, which is shown by the rays of greatest

SOLVENT.	B. Pt.	Refr. Index. D Rays.	t.	SOLUTION OF METASTYROL. Rays transmitted to λ through					Concentration. Gms. per litre.
				1 mm. λ	2 mm. λ	3 mm. λ	5 mm. λ	10 mm. λ	
Chloroform	61°·2 C.	1·4492	15°	2670 2725	2710 2740	2745 2750	2900 2900	3100 3100	4·0
Carbon tetrachloride ...	76°·7	1·4607	20°	2670 2725	2730 2740	2745 2750	2850 2850	3050 3000	4·3
Ethylene dichloride ...	84°·1	1·4472	15°	2670 2725	2720 2740	2730 2750	2900 2850	3100 3100	3·5
Epichlorhydrin	116°·5	1·43969	16°·1	2660	2680	2720	2850 2800	3030 3050	4·3
Toluene	109°·2	1·4955	20°	2980 2950	3000 2960	3030 3000	3050 3050	3260 3300	3·0
Ethylbenzene	134°	1·49559	20°	3030 2960	3050 3000	3440 3350	3500 3500	3600 3600	2·5
Turpentine	153°	1·479	17°·4	2920	2980	3030	3100 3050	3300 3200	1·64
p.-xylene	136°·5	1·4846	16°	2870	2880	2910	2960 2950	3050 3100	4·3
m.-xylene	139°·8	1·5020	15°·5	2900	3000	3040	3100	3250	4·3
Mesitylene	162·6°–163.6°	1·4960	19°	—	—	—	3550	3700	13·3
Pure glycerine only ...	—	—	—	—	—	—	2275	2275	—

The measurements of the transmitted rays were made in duplicate through thicknesses of 5 mm. and 10 mm. by different observers at different times. The figures show slight differences, but it may be presumed that the larger wave-lengths recorded as being the terminations of the several spectra in the ultra-violet are the more correct. It will be seen that the chloroform and epichlorhydrin are liquids very similar in properties, though solutions of metastyrol in the latter transmit rather more of the ultra-violet spectrum, and its boiling point is considerably higher and its volatility therefore much less.

refrangibility transmitted with full intensity through different thicknesses of the liquid; also as regards refractive power and volatility. Furthermore, the absorption spectrum of solid films of metastyrol of different thicknesses was photographed and compared with solutions of the substance in thin liquid films held between two plates of quartz. The results are most conveniently stated in tables, but as an illustration of the mode of examination, the photographic plate is here reproduced upon which the properties of toluene and ethylbenzene are compared. In spectrum 5, the absorption bands characteristic of toluene become visible near the extreme end of the transmitted rays in the ultra-violet.

The properties of solvents and of solutions of metastyrol are tabulated on the preceding page. A solution of metastyrol in alcohol was evaporated to dryness in a quartz capsule, its volume was 10 c.c., the area covered by the dry film was 32 mm. in diameter, in the centre this measured 7·5 μ in thickness. The film detached from the quartz was cut in two and the pieces placed one on the other were cemented together with chloroform. Photographs were taken through this thickness of 15 μ. Through 7·5 μ the rays were transmitted to λ 3100, but were reduced in intensity to the extent of about one-third throughout the visible and ultra-violet; through 15 μ the rays were transmitted to λ 3290. The fluorescence of the film was a pale green and by no means strong. It is highly important in the examination of these substances, especially through different thicknesses, that one may say not only where the rays are cut off but also where they begin to be weakened, and furthermore to be able to demonstrate to what extent they are transmitted with diminished intensity, and with what exposure. For instance, a reference to the photograph plate No. 41, Fig. 3, will render evident in what circumstances as a solvent for metastyrol toluene is to be preferred to ethylbenzene or *vice versâ*. By consulting the tabulated statement it becomes evident why chloroform, carbon tetrachloride and epichlorhydrin are to be preferred to the benzenoid hydrocarbons.

The screen of quinine sulphate may be employed for isolating the line Cd 17, λ 2748·7, the layer of liquid being from 5 mm. to 10 mm. in thickness.

The screen of silver deposited by Edser and Stanfield's process may be used for isolating the Cd line 12, λ 3261·2 or the line of tin λ 3175·1.

POSTSCRIPT.

The author's work was unfortunately interrupted at the beginning of April by a serious illness, and hence he was unable to demonstrate the useful application of these screens for the purposes here suggested.

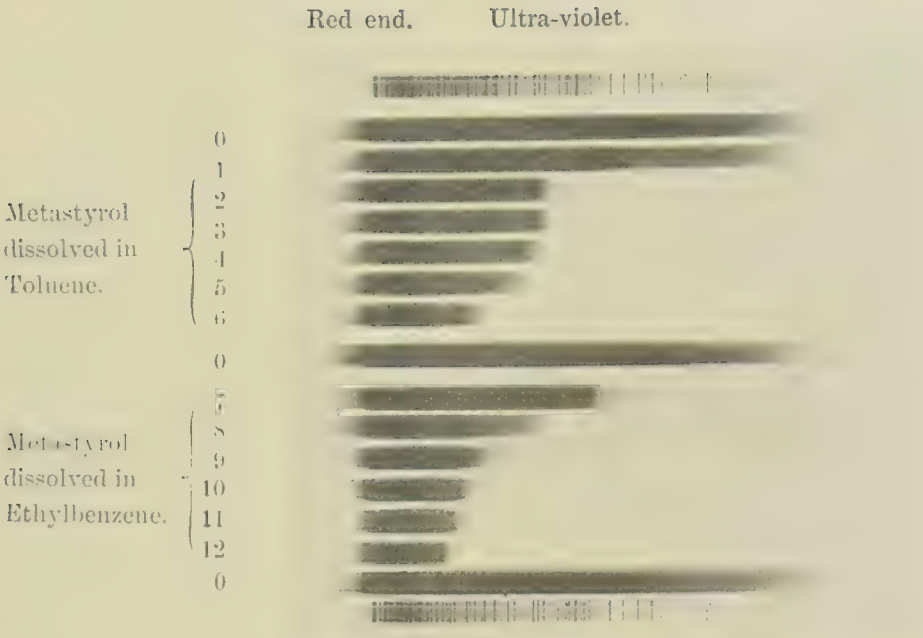


FIG. 3.

Spark lines of cadmium, lead, and tin for reference at top and bottom.

0. The almost continuous spectrum of the uranium spark. 1, 2, 3, 4, 5 and 6, metastyrol in toluene, 0·03 grs. in 10 c.c.

No. 1 shows the rays transmitted through a film held between two quartz plates as in mounting objects. Nos. 2, 3, 4, 5 and 6 are through thicknesses of 1 mm., 2 mm., 3 mm., 5 mm. and 10 mm. respectively.

No. 7 is metastyrol in ethylbenzene, 0·03 gr. in 12 c.c., the thickness being a film between two quartz plates. Nos. 8, 9, 10, 11 and 12 are through 1 mm., 2 mm., 3 mm., 5 mm., and 10 mm. respectively.

The two least refrangible lines conspicuous on the photograph of the spark spectrum in Fig. 3 are in the yellowish-green, and belong to cadmium, with wave-length 5086·1 and 4,800·1.

Sec. IX.—To face page 94.

Sur le traitement simplifié des plaques autochromes et la correction des erreurs de temps de pose au cours du développement.

Par MM. A. et L. Lumière et A. Seyewetz.

(Résumé)

Les auteurs indiquent une méthode simplifiée de traitement des plaques autochromes qui permet d'obtenir sans renforcement des images très vigoureuses lorsque le temps de pose a été exactement apprécié.

Les manipulations ne nécessitent plus que l'emploi de 2 bains et sont réduites alors à 3 opérations; le 1er développement, l'inversion de l'image et le 2e développement.

Les deux développements ont lieu au moyen d'un révélateur à la métoquinone et à l'ammoniaque dont les auteurs donnent la composition et l'inversion est obtenue avec le bain habituel de permanganate de potassium acide.

Les auteurs indiquent en outre une méthode de developpement méthodique à la métoquinone et à l'ammoniaque permettant de corriger les erreurs de temps de pose. Cette méthode est basée sur la durée d'apparition des premiers contours de l'image dans le révélateur convenablement dilué, comme dans la méthode de développement à l'acide pyrogallique à deux bains qu'ils ont indiquée antérieurement.

Dans cette méthode pour éviter des mesures de volume avec le faible éclairage de laboratoire, ils emploient la même quantité de révélateur quel que soit le degré de surexposition (sauf pourtant dans les cas de très forte sous-exposition). Les corrections nécessitées par l'inexactitude, le temps de pose, sont obtenues en faisant varier la durée du développement.

Les auteurs donnent un tableau permettant d'employer très facilement dans la pratique cette méthode de développement.

Discussion.

Mr. Maximilian Toch said : The method which I have devised and which was published before the New York Camera Club on March 23rd relates to this subject inasmuch as I have reduced the method to practically three operations, as follows : 1st, Development in either metol-quinol, pyrogallol, or edenol ; 2nd Reversal; 3rd, Redevelopment in the same developer. The picture need not be fixed but may

be intensified. The best intensifier which I have found is $HgCl_2$ and sulphite of soda.

Working in darkness is not necessary after development has begun ; virida paper or very dark red is perfectly safe.

Mr. A. Watt was pleased to find that when the Lumière plate was first introduced that the time of development was fixed, and thinks that the new method of varying the method of development is a backward step. It would be better to take more trouble to obtain correct exposure. The simplest method, in his opinion, to obtain the correct exposure is to make an exposure and develop on the spot. He showed an apparatus by which this can be done anywhere, where a supply of water can be obtained.

Professor Luther sagte: Um die unrichtige Exposition zu korrigieren, benutzten Lumière und Seyewetz früher die Methode, dass zu jeder Erscheinungszeit eine bestimmte Ammoniakmenge benutzt und eine bestimmte Zeit entwickelt wurde. Um diese Methode zu vereinfachen, habe ich eine Bürette benutzt, aus der in jedem Moment gerade soviel ammoniakalische Flüssigkeit ausgeflossen ist, als die Erscheinungszeit erfordert. Durch weitere Einrichtungen wird die Entwicklung nahezu automatisches und kann mit Leichtigkeit von einem Menschen ausgeübt werden.

M. Seyewetz répondit: On peut obtenir de bons résultats avec d'autres révélateurs que la métoquinone, mais nous avons cherché surtout en indiquant ce révélateur à obtenir les résultats les meilleurs avec les moyens les plus simples.

Le développement à la métoquinone n'exclut pas la possibilité d'employer d'autres révélateurs.

Prof. Namias: Je puis confirmer que la nouvelle méthode de développement à la métoquinone, préconisée récemment par MM. Lumière et Seyewetz donne des résultats qui ne laissent rien à désirer. Avant que cette nouvelle formule fût indiquée j'avais essayé d'autres révélateurs et j'avais recommandé comme excellent un révélateur à base de glicim et métol. Aujourd'hui je ne sais conseiller rien de mieux que le développateur à la métoquinone. C'est une formule très bien étudiée, et après bien d'essais je puis affirmer que peut-être on pourrait obtenir des résultats égaux, mais il est bien difficile d'en obtenir des supérieurs.

Autochromes and their reproduction on Paper.

By Howard Farmer, *Principal of the Photographic School, Polytechnic Institute.*

From the facility with which the colours of natural objects are reproduced on the autochrome plate, it would appear an easy matter to reproduce the colours of autochromes equally well on other autochrome plates, or on paper by means of any of the tri-colour processes.

In practice, however, directly attempts are made to use autochromes as the originals for colour reproductions, baffling defects and irregularities arise, of which the following are examples:—

The chief source of the trouble occurs in the fundamental nature of the autochrome image, by virtue of which its three synthetical colours lie side by side, each one of them occupying a comparatively small portion of the total area of the plate. Consequently a photographic negative from either colour also only occupies a portion of the negative plate; the intermingled portions, which theoretically should be quite transparent, representing the areas occupied by the other colours.

If the theoretical results were obtained in practice, the effect of these intermingled transparent spaces on the values of the gradations of the negatives would be to render the production of negatives from autochromes an absurdity. But lens aberrations and variations in the irradiation constant of sensitive films, which, owing to the minuteness of the areas in which they operate, pass unheeded in ordinary photographic work, give rise to an extensive spreading of the silver deposits, which therefore fill more or less the intermingled spaces. The practicability of the reproduction of autochromes is entirely dependent upon the ordered control of this spreading.

The following are some devices for attaining these conditions which have been tested at the Polytechnic:—

1.—By irradiation in the sensitive film.

2.—By interposing an air space or transparent film between the autochrome film and the sensitive film, when producing negatives in the printing frame.

3.—An intentional diffusion of focal definition when negative making in the copying camera.

4.—An intentional to-and-fro or lateral movement of the plate lens or autochrome during exposure.

5.—Imparting a vibratory motion to the copying camera or easel carrying the autochrome.

6.—The use of a diffusing glass or lens.

7.—Placing a piece of finely-ground glass in contact with the sensitive film or autochrome.

8.—Interposing a thin plate of glass between the autochrome and the image, and slightly oscillating the glass during exposure. (I am indebted to Prof. W. Hibbert for the suggestion of this valuable method).

9.—Placing a fine ruled screen in contact with the sensitive film. (The mode of action of this device has already been published.)

10.—By a current of irregularly heated air passing in front of the lens.

The employment of these or other devices does not necessarily mean a loss of visual definition. The autochrome itself does not show any appreciable loss of visual definition due to its irregularly coloured starch grain texture. A patch of red, for example, appears to the unaided eye as a solid patch of colour, whereas in fact it is both grained and mottled. What we require is that the reproduction should represent, not the dissected anatomy of the autochrome, but what the eye sees when looking at it.

Attached to this paper were some experimental examples of chromo-typography, produced with the aid of the devices referred to.

Discussion.

Prof. NAMIAS dit : J'ai lu la brochure de Mr. H. Farmer et j'ai vu qu'il indique plusieurs moyens pour produire la sélection des trois couleurs de l'image autochrome. Mais il ne dit pas laquelle de ces méthodes il a appliqué pour obtenir les belles épreuves imprimées qu'il a présentées au Congrès. C'est surtout là ce que je désirerais savoir.

WELLCOME LIBRARY INSTITUTE

PRINTED BY
JAS. TRUSCOTT & SON, LTD.,
SUFFOLK LANE, LONDON, E.C.